A DICTIONARY

OF

APPLIED CHEMISTRY

VOL. I.

A DICTIONARY OF APPLIED CHEMISTRY

BY

SIR EDWARD THORPE, C.B., LL.D., F.R.S.

Assisted by Eminent Contributors

REVISED AND ENLARGED EDITION

5 Vols.   Medium 8vo, £2 5*s*. net per volume.

LONGMANS, GREEN, AND CO

LONDON, NEW YORK, BOMBAY, AND CALCUTTA

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OF

APPLIED CHEMISTRY

BY

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CHEMICAL SOCIETY AND OF THE SOCIETY OF CHEMICAL INDUSTRY

ASSISTED BY EMINENT CONTRIBUTORS

IN FIVE VOLUMES

VOL. I.

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WITH ILLUSTRATIONS

LONGMANS, GREEN, AND CO.
89 PATERNOSTER ROW, LONDON
NEW YORK, BOMBAY, AND CALCUTTA
1912

PREFACE

During the twenty-two years that have elapsed since the first volume of this work made its appearance, chemistry has advanced at a rate and to an extent altogether unprecedented in its history, or, indeed, in the history of any other science. This extraordinary growth has been accompanied by a no less remarkable increase in the variety and comprehensiveness of its applications to the arts and manufactures. Accordingly, in the attempt to make this re-issue reasonably adequate as a presentation of contemporary knowledge, both as regards the science and its applications, it has been found absolutely necessary to enlarge greatly the original scope of the book. All the articles in the former issue have been carefully revised and many have been wholly rewritten. In addition, of course, a large number of new and important subjects have had to be dealt with. The result is that this edition of the Dictionary of Applied Chemistry is practically a new work.

In preparing it the Editor has again been fortunate in securing the co-operation of eminent authorities, not only in the United Kingdom, but also in America, Germany, Switzerland, etc., as writers on subjects with which they are specially qualified to treat. A list of these, with the titles of their contributions, is prefixed to the several volumes in which these contributions appear. Their names and standing are a sufficient guarantee that no pains have been spared to make the work a faithful record of the present relations of chemistry to the arts and manufactures.

The Editor desires to express his acknowledgments to the following Demonstrators, Assistant-Demonstrators, and Assistants in the Chemical Department of the Imperial College of Science and Technology for help in the revision and compilation of the subject-matter of many of the articles: Dr. W. N. Haworth; Dr. H. F. Harwood, M.Sc.; Dr. P. W. Robertson, M.A., M.Sc.; Dr. Arthur Clayton; Mr. A. T. King, B.Sc.; Mr. H. V. A. Briscoe, B.Sc.; Mr. E. G. Couzens, B.Sc.; Mr. F. P. Dunn, B.Sc.; Mr. H. F. V. Little, B.Sc.; and Mr. J. A. Pickard, B.Sc. Also to Mr. Arthur G. Francis, B.Sc., of the Government Laboratory; Mr. Lionel M. Jones, B.Sc., of the Birmingham Technical School; Miss Zelda Kahan, B.Sc., and Miss Gertrude Walsh, M.Sc.

Lastly, he is under great obligations to Dr. M. A. Whiteley, A.R.C.S., and Mr. F. P. Dunn, B.Sc., A.R.C.S., of the Imperial College, for the care and attention they have bestowed on the revision of the proof-sheets, and for the assistance they have rendered generally in the production of the work.

ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Annalen der Chemie (Justus Liebig).
Ann Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur.	Annales de l'Institut Pasteur.
Arch. Pharm.	Archiv der Pharmazie.
Bentl. a. Trim.	Bentley and Trimen. Medicinal Plants.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Brewers J.	Brewers Journal.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Soc. Proc.	Journal of the Chemical Society of London. Proceedings.
Chem. Soc. Trans.	Journal of the Chemical Society of London. Transactions.
Chem. Zeit.	Chemiker Zeitung.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Dingl. poly. J.	Dingler's polytechnisches Journal.
Färber-Zeit.	Färber-Zeitung.
Flück. a. Hanb.	Flückiger and Hanbury. Pharmacographia.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.
Gazz. chim. ital.	Gazzetta chimica italiana.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Phys. Chem.	Journal of Physical Chemistry.
J. pr. Chem.	Journal für praktische Chemie.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers.	Journal of the Society of Dyers and Colourists.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pharm. J.	Pharmaceutical Journal.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society.
Phot. J.	Photographic Journal.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs-und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

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A

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AAL, A′L, ACH, AI′CH. Native names for the roots of *Morinda tinctoria* and *M. citrifolia*, employed in various parts of India, under the general trade name of Suranji, as a dyestuff, more especially for dyeing reds, purples, and chocolates.

ABACA. A species of fibre derived from *Musa textilis* (Née), obtained mainly from the Philippine Islands, and used in the manufacture of mats, cordage, &c. It is also known under other names, including ' Manilla hemp,' ' Menado hemp,' ' Cebu hemp,' ' Siam hemp,' and ' White rope.' Less valuable fibres are obtained from other species of *Musa*, such as *M. sapientum* (Linn.), the banana and plantain, which yield banana fibre and plantain fibre.

ABIES. The generic name of the Silver Firs. *A. alba* (Mill.) [*A. pectinata* (DC.)] furnishes timber very similar to the white deal of *Picea excelsa*, the common spruce. It is the source of 'Strasburg turpentine,' containing free *abienic*, *abietric*, and *α-* and *β-abietinolic acids*, and an amorphous substance *abietoresen*, an ethereal oil of agreeable aromatic odour, a bitter principle and colouring matter (Tschirch und Weigel, Arch. Pharm. 1900, 238, 411).

A. Canadensis is the source of Canada balsam, which contains *canadic*, *canadolic*, and *α-* and *β-canadinolic acids*, an ethereal oil, *canadoresen*; and small quantities of succinic acid and a bitter substance. The acids contain no methoxyl groups and give the cholesterol reactions, including that of Tschugaeff (*l.c.* 1900, 238, 487).

ABIETENE. A hydrocarbon obtained by distilling the terebinthinate exudation of *Pinus sabiniana* (Doug.), a coniferous tree indigenous to California, and growing on the dry slopes of the foothills of the Sierra Nevada and on the hills along the coast, and known locally as the Nut pine or Digger pine. To procure the exudation, the tree during winter is notched and guttered at a convenient height from the ground, and the resin on distillation yields the liquid hydrocarbon. The crude oil was met with in San Francisco as an article of commerce under the names of ' Abietene,' ' Erasine,' ' Aurantine,' and ' Thioline,'

and was used for removing grease-spots, paint-stains, &c., from clothing. It is a nearly colourless mobile liquid of powerful aromatic smell, recalling that of oil of oranges.

Abietene has been shown by Thorpe to consist almost entirely of *normal heptane*, (C_7H_{16}, mixed with a small quantity of a resin to which its characteristic smell of orange oil is due (Thorpe, Chem. Soc. Trans. 35, 296 ; Schorlemmer and Thorpe, Phil. Trans. 174, 269 ; *v.* also Blasdale, J. Amer. Chem. Soc. 1901, 162).

Abietene is also the name given to the hydrocarbon which is obtained as an oil by the reduction of abietic acid (*q.v.*) (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1238 ; Kraemer and Spilker, Ber. 1899, 2953, 3614). Its formula is $C_{18}H_{28}$, and it is probably decahydroretene, as, when carefully purified, and reduced with phosphorus and hydriodic acid, it yields a fluorescent hydrocarbon identical with the dodecahydroretene of Liebermann and Spiegel (Ber. 1889, 780).

ABIETIC ACID. An acid obtained by digesting colophony with dilute alcohol and recrystallising the product from methyl alcohol (Maly, Annalen, 129, 54 ; 132, 249) ; or by saturating an alcoholic solution of colophony with hydrogen chloride and subsequently recrystallising the product (Flückiger, J. 1867, 727). It can also be obtained by distilling colophony under reduced pressure or with superheated steam (Easterfield and Bagley, Chem. Soc. Trans. 1904, 1238). It occurs in resin spirit, from which it may be obtained by extraction with ether, shaking with sodium carbonate solution and then acidifying with acid. It is obtained in a purer condition by recrystallising from acetic acid ; m.p. 166°–167° (Tschirch and Wolff, Arch. Pharm. 1907, 1) ; 153°–154° (Mach, Monatsh. 1893, 186). According to Easterfield and Bagley and Mach, it is a derivative of phenanthrene, and has the formula $C_{19}H_{28}O_2$, whilst Levy (Ber. 1906, 3043), Koritschoner (J. Soc. Chem. Ind. 1907, 641), Fahrion (J. Soc. Chem. Ind. 1907, 264), and Vesterberg (Ber. 1907, 120) represent its composition as $C_{20}H_{30}O_2$. According to Strecker

B

(Annalen, 150, 131), Duvernoy (Annalen, 148, 143), and Easterfield and Bagley (*l.c.*), abietic acid is identical with sylvic acid; it is not identical with pimaric acid, which yields abietic acid on distillation under reduced pressure. By distilling abietic acid under ordinary pressure, or, better, by treatment with hydriodic acid, carbon dioxide is evolved, the hydrocarbon *abietene* $C_{18}H_{28}$ being formed (E. and B. *l.c.*; Levy, *l.c.*; Kraemer and Spilker, Ber. 1899, 3614). Distillation with sulphur converts abietic acid into retene, $C_{18}H_{18}$ (E. and B., *l.c.*; Vesterberg, Ber. 1903, 4200). Oxidation with potassium permanganate yields an acid $C_{10}H_{16}O_3$, m.p. 123° (Mach, Monatsh. 1894, 627); and a method has been devised by Endemann (D. R. P. 183328; Chem. Zentr. 1907, i. 1607) to oxidise resinous materials, containing abietic acid, to resin acids and malonic acid.

Detection and Estimation.—The following colour reactions may be used for detecting abietic acid:—(1) 3 vols. of conc. hydrochloric acid and 1 vol. of ferric chloride sol. give a violet red colouration; (2) sulphuric acid dissolves abietic acid to a red solution; (3) when heated with dry chloroform, acetic anhydride and sulphuric acid, a purple red colour is produced changing through violet and blue to a greenish black (Mach. *l.c.*). In order to estimate abietic acid in resins, &c., 10 grms. of the substance are refluxed with 20–25 c.c. of 10 p.c. alcoholic potash for ¼ hour on a water-bath; the resulting soap is decomposed with dilute hydrochloric acid, and the separated resin filtered off, washed with cold water and dried. It is then powdered and extracted with 50 c.c. of hot petroleum ether. From this solution abietic acid is precipitated by ammonia, filtered off, dried on the water-bath, and the ammonia expelled by gentle heating. The residue represents the amount of crude abietic acid in the sample (Rebs, Chem. Zentr. 1907, i. 997).

Abietic acid (or colophony) is used in assisting the growth of lactic or butyric ferments, as it favours the production of that which is present in the greater quantity and suppresses the other. It promises to be of great use in the fermentation industry in preventing infection (Effront, Compt. rend. 136, 1556), (*v.* COLOPHONY).

ABRASIVES. The various hard substances, chiefly of mineral origin, used for abrasive purposes fall naturally into the following groups, in which the hardness is roughly inversely proportional to the complexity of chemical composition.

Elements.—Diamond (*q.v.*) is the hardest of all substances (hardness = 10 on Mohs's scale). Inferior material of no use for gems is known as b o a r t (or bort), and is crushed to powder and much used by lapidaries. Diamond powder is the only material with which diamond itself can be ground and polished. Embedded in the edge of a thin disc of soft iron, diamond powder is largely used for cutting gem-stones and thin sections of rock specimens, and also for slicing larger blocks of the harder ornamental stones. A black, compact variety of diamond known as c a r b o n a d o ('carbonate' or 'carbon') is embedded in the steel crowns of rock-drills.

Amongst artificial products, steel and some other hard metals are used for abrasive purposes.

The so-called crushed steel, made by quenching white-hot crucible steel, is used in the stone cutting trade. Tantalum is an extremely hard metal and may in future find some application depending on hardness.

Carbides.—Carborundum[1] (*q.v.*) or silicon carbide, CSi (H. = 9½), is prepared artificially in the electric furnace from petroleum-coke and the purest quartz-sand, and is produced in large quantities (over 3000 tons in 1907) at Niagara Falls. It is largely made into sharpening stones and grinding wheels. In lapidaries' work it has to a certain extent taken the place of corundum: but although harder than corundum, it has the disadvantage of being more brittle, and it soon rubs to flour. Carbide of boron, CB_6, and silicide of boron, SiB_3, are also remarkable on account of their intense hardness (H. Moissan, Compt. rend. 118, 556).

Oxides.—Corundum (*q.v.*) Al_2O_3 is, next to diamond, the hardest of minerals (H. = 9). The impure variety, emery (*q.v.*), is not quite so hard. The crushed and graded material is made into corundum wheels and emery paper, and is much used in lapidaries' work. Artificial corundum, known by the trade-name of 'alundum,' is now manufactured in considerable amounts (about 3000 tons in 1907) at Niagara Falls, by fusing bauxite in an electric furnace. 'Corubin' is also an artificial corundum, formed as a by-product in the Goldschmidt thermite process.

Quartz (*q.v.*) SiO_2 (H. = 7), and its several varieties find extensive applications. Millstones and grindstones are made of quartz-rock, quartzite, burrstone (or buhrstone), grit, or sandstone (*q.v.*); while scythe-stones, oilstones (*q.v.*), and whetstones (*q.v.*) consist of hornstone, lydian-stone and other compact varieties of quartz. In the form of sand, quartz is used as a sand-blast, in scouring-soap, for cutting and grinding marble, making sand-paper, &c. Tripoli or infusorial earth is a powdery variety of opal (hydrated silica), and is used for polishing.

Silicates.—Garnet (*q.v.*) (H. = 6½–7½) is used for making 'emery' paper and cloth: and felspar (*q.v.*) (H.=6) is also used to a small degree. Silicate rocks are employed to a small extent; *e.g.* pumice for polishing, and the millstone lava (leucite-nepheline-tephrite) of Niedermendig on the Rhine, for millstones. L. J. S.

ABRASTOL or *Asaprol - Etrasol.* Trade names for the calcium salt of β-naphtholsulphonic acid, $Ca(C_{10}H_7OSO_3)_2,3H_2O$, used in the clarification and preservation of wines. The maximum quantity needed for this purpose is 10 grms. per hectolitre. According to Noelting and Dujardin-Beaumetz and Stackler, the substance is harmless from a hygienic point of view (see Mon. Sci. 1894, 8, 257; J. Soc. Chem. Ind. 1894, 177, 534). To detect its presence, Sanglé-Ferrière proceeds as follows (Compt. rend. 1893, 117, 796): 200 c.c. of the wine is boiled for an hour in a reflux apparatus with 8 c.c. of hydrochloric acid, when the abrastol is hydrolysed to β-naphthol, which may be extracted with benzene, and the residue left after distilling the benzene sol. taken up with chloroform. A fragment of potash is dropped

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[1] So named by E. G. Acheson, in 1893, from carbon and corundum, because before it had been analysed, it was thought to be a compound of carbon and alumina.

into the chloroform solution, which is boiled for 2 mins., when a blue colouration is produced changing to green and finally becoming yellow. 0·1 grm. per litre may thus be detected. The presence of abrastol in no way vitiates the determination of potassium sulphate (J. Soc. Chem. Ind. 1894, 177). Sinibaldi (Mon. Sci. 7, 842) has given the following method : 25 c.c. of the wine are neutralised by ammonia and shaken with 25 c.c. of amyl alcohol. After separation, the amyl alcohol is boiled to expel ammonia, and when cold is shaken with 0·25 c.c. ferric chloride sol. A grey-blue colouration denotes abrastol. Gabutti (Chem. Zentr. 1904, 2, 370) proceeds in a similar way, but instead of ferric chloride, employs phosphoric acid and formaldehyde solution, when, in presence of abrastol, a green fluorescence is produced. (For other methods, v. Sanna Pintus, J. Soc. Chem. Ind. 1900, 933 ; Briand, Compt. rend. 1894, 118, 925 ; Carletti, Chem. Zentr. 1909, 2, 72. For colour reactions, v. Barral, J. Pharm. Chim. 1903, 18, [5] 206; Salomone, Chem. Zentr. 1907, i. 306.)

(For a review of the various methods of detection, v. Vitali, Apoth. Zeit. 1908, 23, 507 ; J. Soc. Chem. Ind. 1908, 830.)

ABRAUM SALTS. (Ger. *Abraumsalze* : ' salts to be removed.') The mixed salts found overlaying the rock-salt deposit at Stassfurt, in Prussia. These consist mainly of rock-salt ; *Carnallite,* a double chloride of potassium and magnesium ; *Sylvine,* or potassium chloride ; and *Kieserite,* or magnesium sulphate, v. POTASSIUM.

ABRIN. A brownish yellow soluble substance obtained from the seeds of *Abrus precatorius* (*Indian liquorice* or *Jequirity*). Contains a poisonous proteid, resembling, if not identical with, ricin. Lethal dose, according to Kobert, is only 0·00001 grm. per kilo body-weight : *i.e.* 1 to 100,000,000.

ABSINTH. (*Absinthe,* Fr. ; *Wermuthextract,* Ger.) One of the best-known liqueurs or cordials (*q.v.*), is made chiefly at Lyons, Montpellier and Pontarlier in France, and until quite recently (*vide infra*) at Neufchâtel in Switzerland. It is a highly intoxicating spirituous liquor flavoured with oil of wormwood (*Artemisia absinthium,* nat. ord. *Compositæ*) and other essential oils as angelica, anise, cinnamon, cloves, fennel, hyssop, peppermint, &c. (*v.* OILS, ESSENTIAL).

There are three distinct processes in the manufacture of absinth, viz. : maceration, distillation, and colouration. The leaves and flower-tops of *Artemisia absinthium,* together with the other flavouring ingredients (which vary in kind and quality according to the requirements of the different manufacturers) are digested with spirit for periods varying from 12 hours to 10 days, according to the temperature of the infusion and the strength of the spirit used. The French manufacturers, as a rule, digest for short periods at the temperature of an ordinary water bath, and with spirit containing about 85° alcohol, whilst the Swiss maceration process was conducted at air temperature with spirit somewhat below British ' proof ' strength, or about 50° alcohol.

The infusion is distilled and the distillate transferred to the colouring vessel containing small absinth leaves, balm and hyssop, dried and finely divided. This vessel is hermetically sealed and

is gently heated by steam to a temperature of 60° in order to extract chlorophyll. After cooling, the green liquor is drawn off, and strained, if necessary, through a hair sieve. The colouring is sometimes separately prepared and added as required to the colourless distillate. Occasionally the latter is sweetened by the addition of about 5 p.c. by weight of crushed white sugar. Chlorophyll for imparting the green colour to absinth (and other liqueurs) is frequently obtained from nettles, parsley, and spinach, and is free from objection provided the vegetable matter is sound.

On keeping, genuine absinth assumes the yellowish tint appreciated by connoisseurs, and its qualities generally are improved by age. Many objectionable varieties of absinth are, however, on the market, made from inferior spirit, to which essences and resins are added, the former to give a fictitious flavour and the latter to produce the opalescence which occurs in genuine absinth on the addition of water, owing to the liberation of the essential oils, resinous bodies, and colouring matters derived from the plants and seeds used in its manufacture. Other colouring matters than chlorophyll are also employed, as indigo, sulphate of copper, picric acid and turmeric or other vegetable colour. Gum benzoin, aldehyde and rosin are also used to produce ' milkiness ' on dilution, and even chloride of antimony is said to have been employed for this purpose.

To detect adulteration it is usually sufficient to determine the essential oils, resins, and colouring matters (*vide* Hubert, Ann. Chim. anal. 6, 409, and Nivière and Hubert, Mon. Sci. 1895, 566). According to Hubert, absinth has a specific gravity of 0·8966 to 0·9982, and alcoholic strength of 47 to 72 p.c. by volume of absolute alcohol. The average results of twelve samples expressed as grams per litre were as follows : essential oils, 1·5 to 5·0 ; extractive, 0·36 to 1·72 ; acids, 0·024 to 0·288; aldehydes, 0·005 to 0·155; furfurol, 0·0002 to 0·007 ; ethers, 0·005 to 0·123. The strength of absinth as imported into the United Kingdom varies from ' proof ' to about 20 over proof, and rather more than 3000 gallons are imported annually.

Although genuine absinth, taken in moderation, has valuable qualities as a cordial, stomachic, and febrifuge, its characteristic bitter principle, absinthiin (*q.v.*), is an active poison, having a very injurious effect upon the nervous system of those addicted to the habitual and immoderate consumption of absinth. Legal measures have therefore been taken in various European countries to control, restrict, or even prohibit its sale. In France, liqueurs may not contain more than 1 gram per litre of oil of wormwood or other oil of similar toxic nature, whilst in Belgium the manufacture and sale of absinth have been entirely prohibited. A similar prohibition was enforced in 1910 by the Swiss Government. J. C.

ABSINTHIN or **ABSINTHIIN** $C_{15}H_{20}O_4$. The bitter principle extracted from the dried leaves of large absinth or wormwood (*Artemisia absinthium*) is an active poison. and it is to its presence in oil of wormwood that the toxic effect of absinth (*q.v.*) appears to be due.

Various formulæ have been ass...

substance, the differences being due to the difficulty of obtaining it in a pure state (Mein, Annalen, 8, 61; Luck, Annalen, 78, 87; Kromayer, Arch. Pharm. [2] 108, 129).

Pure crystallised absinthiin was first isolated by Duquesnel (Bul. de Therapeutique, 107, 438). Senger obtained absinthiin as a pale yellow amorphous substance melting at 65° and having the empirical formula $C_{15}H_{20}O_4$. This formula was confirmed later by Bourcet, who found that the pure substance crystallises in fine white prismatic needles melting at 68°, the amorphous form and lower melting-point found by Senger being probably due to traces of a resinous impurity.

According to Senger and Bourcet, absinthiin is a glucoside, free from nitrogen, and is decomposed by the action of dilute acids, or even by boiling with water, into dextrose, a volatile oil, and a solid resinous body of the aromatic series. It is soluble in alcohol, ether, chloroform, or benzene: difficultly soluble in light petroleum, water, though more soluble in cold than in boiling water. It gives a precipitate with tannic acid and with gold chloride, which is reduced on warming; yields volatile fatty acids on oxidation with nitric acid, and oxalic and picric acids with potassium chromate and sulphuric acid. With Fröhde's reagent it gives a brown colour, changing to violet, then blue; and with sulphuric acid brown, passing through green to blue (Senger, Arch. Pharm. 230, 103; and Bourcet, Bull. Soc. chim. [3] 19, 537).   J. C.

ABSINTHOL $C_{10}H_{16}O$. The essential principle of oil of wormwood derived from *Artemisia absinthium* (nat. ord. *Compositæ*), a plant indigenous to most European countries and comparatively recently introduced into the United States of America, whence increasing supplies of the cheaper qualities of wormwood oil are now obtained.

Although the oil obtained by the distillation of wormwood has been known for at least four centuries, its chemical composition was first systematically investigated in 1845, when Leblanc (Compt. rend. 21, 739) showed that its principal constituent, boiling at 203°, has the formula $C_{10}H_{16}O$. This was confirmed later by Gladstone and other investigators (Chem. Soc. Trans. 17, 1), and by Beilstein and Kupffer (Annalen, 170, 290), who gave to the product the name '*absinthol*,' and identified its dehydration product with *cymene*.

Semmler (Ber. 25, 3350) proved absinthol to be a ketone identical with thujone or tanacetone, which occurs largely in other essential oils, as oil of tansy, sage, and *Artemisia barelieri*. It is a colourless oily liquid of pleasant odour, strongly dextrorotatory (about $+68°$), boils at 203°, density 0·9126 at 20°, and refractive index 1·4495.

Though isomeric with camphor, it differs from that body in combining with sodium bisulphite and in not being converted into camphoric acid by means of nitric acid, nor into camphocarboxylic acid by treatment with carbon dioxide and sodium. With melted potash it gives a resin, but no acid. When heated with P_2S_5 and $ZnCl_2$ it yields cymene (Beilstein and Kupffer, Ber. 6, 1183; Annalen, 170, 290; Wright, Chem. Soc. Trans. 27, 1 and 319; Semmler, Ber. 25, 3343 and 27, 895).   J. C.

ABUTILON INDICUM (Sweet), **PETAREE** or **TUBOCUTY.** The bark of this malvaceous tree consists of long, thin, tough fibrous strips (bast fibres), and, according to Dymock (Pharm. J. [3] 8, 383) and others, is worthy of attention as a source of fibre.

ABYSSINIAN GOLD. A yellow alloy of 90·7 parts of copper and 8·3 of zinc. The ingot is plated on one side with gold, and is then rolled out into sheets, from which articles of jewellery are formed in the usual way, the amount of gold on the finished article varying from 0·03 to 1·03 p.c. Known also as *Talmi gold*. The term is sometimes applied in trade to Aluminium Bronze.

ACACIA CATECHU (Willd) or **KHAIR** is a tree growing in various parts of India. Its unripe pods and wood, by decoction, yield a catechu (Agricult. Ledger, 1895, No. 1, and 1896, No. 35) known by the name of Cutch or Kutch, which must not be confounded with the officinal catechu (*Catechu pallidum*). It is used in the preparation of some leathers and by dyers. The timber is also used for constructional and other purposes.

ACACIA GUM *v.* GUMS.

ACANTHITE. A form of silver sulphide found at the Enterprise mine, near Rico, in black crystals of orthorhombic habit (Chester, Zeitsch. Kryst. Min. 1896, 26, 526).

ACAROID RESIN or **BOTANY BAY RESIN** *v. Xanthorrhœa Balsams,* art. BALSAMS.

ACCIPENSERINE. A protamine belonging to the sturine group found in the testis of *Accipenser stellatus.* Composition of the sulphate: $C_{35}H_{72}O_9N_{18}, 4H_2SO_4$ (Kuracéff, Zeitsch. physiol. Chem. 1901, 32, 197).

ACENAPHTHENE $C_{12}H_{10}$, *i.e.* $C_{10}H_6 : C_2H_4$. A crystalline substance found in coal-tar oil (Berthelot, Bull. Soc. Chim. [2] 8, 226). Obtained by cooling the fraction of heavy coal-tar oil boiling between 260° and 270°. On recrystallising the solid product from alcohol, acenaphthene is obtained in long needles, m.p. 95° (Behr and Dorp, Annalen, 172, 265), 103° (Schiff, Annalen, 223, 263); b.p. 278°; 229·5° (Perkin, Chem. Soc. Trans. 69, 1196).

For its Absorption Spectrum, *v.* Baly and Tuck (Chem. Soc. Trans. 1908, 1902); Heats of Solution (Speyers, Amer. Chem. J. 18, 146); Magnetic Rotation (Perkin, Chem. Soc. Trans. 1896, 1088); Refraction and Dispersion (Pellini, Gazz. chim. ital. 31, i. 1); Similarity in form to acenaphthylene (Billows, Chem. Zentr. 1903, ii. 44).

Is reduced by hydrogen in presence of nickel to tetrahydroacenaphthene (Sabatier and Senderens, Compt. rend. 132, 210, and 566); with NiO_2 to tetrahydro- and dekahydroacenaphthene (Ipatjew, Ber. 41, 997).

With potassium dichromate and acetic acid yields naphthalic acid and acenaphthenequinone (Graebe and Gfeller, Ber. 25, 652; Jaubert, Gazz. chim. ital. 25, i. 245).

Derivatives.--Oxygenated (Graebe and Gfeller, Annalen, 276, 1; Hodgkinson, Chem. Soc. Proc. 1896, 110); with sulphur (Dziewonski, Ber. 36, 962; Rohlander, Ber. 36, 1583): styphnate (Gibson, Chem. Soc. Trans. 1908, 2098).

ACETAL $C_6H_{14}O_2$, or $CH_3 \cdot CH(OC_2H_5)_2$ (Döbereiner, Gm. 4, 805; Liebig, Annalen, 5, 25; 14, 156; Stas, Ann. Chim. Phys. [3] 19, 146;

Wurtz, Ann. Chim. Phys. [3] 48, 70 ; Geuther, Annalen, 126, 63).

To prepare acetal by Wurtz's method, 2 parts alcohol are added to a mixture of 3 parts manganese dioxide, 3 parts sulphuric acid and 2 parts water, and, after the effervescence first produced has subsided, the whole is heated at 100° until 3 parts have distilled over. The product is then fractionally distilled, and two portions, one boiling below 80° and the second boiling at 80°–95°, are collected.[1] Each fraction is treated with solution of calcium chloride and the ethereal layer which separates is distilled. The product contains aldehyde and ethyl acetate in addition to acetal; to remove these it is shaken with concentrated aqueous potash, the brown liquid separated from the aqueous layer is distilled, and the distillate shaken with calcium chloride. It is then heated with twice its volume of concentrated aqueous soda in sealed tubes at 100° for 24 hours, separated from the soda, distilled, the distillate again rectified : the fraction 100°–105°, which constitutes the greater portion, is acetal.

In addition to its formation as a by-product in the oxidation of alcohol, acetal can also be obtained from a mixture of acetaldehyde (1 vol.) and absolute alcohol (2 vols.) (1) by heating with acetic acid ($\frac{1}{2}$ vol.) for 12 hours at 100° (Geuther, Annalen, 126, 63) ; (2) by cooling in a freezing mixture, passing dry hydrogen chloride to saturation, and decomposing the resulting monochlorether with sodium ethoxide (Wurtz and Frapolli, Compt. rend. 67, 418 ; Annalen, 108, 223) ; or (3) by cooling a mixture of equal volumes to −21°, and passing a current of pure hydrogen phosphide for 24 hours (Engel and Girard, Compt. rend. 92, 692 ; J. 1880, 694).

Acetal is a colourless liquid with agreeable odour : b.p. 104°, and sp. gr. 0·821 at 22·4° (Stas, Annalen, 64, 322) ; b.p. 103·7°–104·3° at 744·4 mm., and sp. gr. 0·8314 at 20°/4° (Brühl, Annalen, 203, 25). It is soluble in 18 vols. of water at 25°, and the solubility increases as the temperature rises. Acetal is miscible in all proportions with alcohol and ether, does not reduce ammoniacal silver solution, and is unaltered on exposure to air ; platinum black, however, oxidises it first to acetaldehyde and subsequently to acetic acid.

Acetal does not give the iodoform reaction until shaken with a few drops of hydrochloric acid, whereby the acetal is hydrolysed to alcohol and aldehyde.

Derivatives.—Mono-, di-, and trichloracetal are obtained as intermediate products in the preparation of chloral by passing chlorine through 80 p.c. alcohol (Lieben, Ann. Chim. Phys. [3] 52, 313 ; Paternò, Compt. rend. 67, 765). According to Krey (J. 1876, 475), a better yield of these derivatives is obtained if a mixture of 2 parts absolute alcohol, 3 parts manganese dioxide, 3 parts sulphuric acid, and 2 parts water is heated until $\frac{2}{3}$ of the liquid has distilled over and chlorine is passed through the well-cooled distillate until it shows signs of turbidity. In either case the product is washed with water, dried over calcium chloride, and submitted to fractional distillation. The fraction 80°–120°

contains chiefly aldehyde and compound ethers, 120°–170° chiefly monochloracetal, 170°–185° dichloracetal (Lieben, *l.c.*), and the fraction boiling above 185° contains trichloracetal (Paternò, *l.c.*). These compounds may then be obtained in the pure state by repeated fractionation.

A better method of obtaining monochloracetal is by passing chlorine through well-cooled 94–99 p.c. alcohol until the chlorinated product has a sp.gr. 1·02–1·03 at 25°. Half the original volume of alcohol is added and the mixture heated a few hours at 50°–60°. The free acid is removed by calcium carbonate ; the oil washed with water, dried and fractionated. The proportion of di- and tri- chloro-derivatives formed depends on the amount of chlorine added (Fritsch, Annalen, 279, 288).

Monochloracetal $CH_2Cl.CH(OC_2H_5)_2$ (Lieben, Annalen, 146, 193 ; Paternò, Mazzara, Ber. 6, 1202 ; Klien, J. 1876, 336 ; Natterer, Monatsh. 3, 444 ; 5, 497 ; Wislicenus, Annalen, 192, 106 ; Frank, Annalen, 206, 341) is a colourless liquid, having an aromatic ethereal odour ; b.p. 155° ; sp.gr. 1·0418 at 0°, 1·026 at 15° (Klien) : 156°–158° (Autenrieth, Ber. 24, 159). When heated with bleaching powder it yields di- and trichloracetal, chloroform, and chlorinated acetaldehyde (Goldberg, J. pr. Chem. [2] 24, 107).

Dichloracetal $CHCl_2.CH(OC_2H_5)_2$ (Jacobsen, Ber. 4, 217 ; Pinner, Ber. 5, 148 ; Annalen, 179, 34 ; Krey, *l.c.* ; Paternò, Annalen, 149, 372 ; 150, 134) : b.p. 183°–184° ; sp.gr. 1·1383 at 14°. When treated with hydrocarbons it forms compounds of the type $CHX_2.CCl$ (Fritsch, Annalen, 279, 219 ; Wiechell, Annalen, 279, 337 ; Buttenberg, Annalen, 279, 324).

Trichloracetal $CCl_3.CH(OC_2H_5)_2$ (Byasson, Bull. Soc. chim. 32, 304 ; Wurtz, Frapolli, J. 1872, 438) ; b.p. 197° ; 204·8° at 758·7 mm. Paternò, Pisati J. 1872, 303) ; sp. gr. 1·2813. When heated with concentrated sulphuric acid it yields chloral.

Trichloracetal $C_8H_{11}Cl_3O_2$. Obtained by the action of chlorine on alcohol (Lieben, Paternò, Krey, *l.c.*) ; crystallises in monoclinic needles resembling caffeine ; m.p. 89°.

Monobromacetal (Pinner, Ber. 5, 149 ; Wislicenus, Annalen, 192, 112 ; Fischer a. Landsteiner, Ber. 25, 2551 ; Freundler a. Ledru, Compt. rend. 1905, 140, 794) ; b.p. 81°–82° at 27–28 mm. (Freundler). According to F. a. L. a cheap method of making monobromacetal is by brominating paraldehyde at 0° with constant shaking ; mixing with absolute alcohol, and after standing 12 hours pouring into an ice-cold sol. of potassium carbonate. The separated oil is dried and fractionated *in vacuo*.

Monoiodoacetal, b.p. 100° at 10 mm. ; sp. 1·4944 at 15° (Hesse, Ber. 1897, 30, 1438).

ACETALS (Wurtz, Ann. Chim. Phys. [3] 48, 370). The acetals are a group of compounds formed by the combination of 1 mol. of an aldehyde with 2 mols. of an alcohol, and the elimination of the elements of 1 mol. of water. They are generally obtained as by-products in the preparation of aldehydes by the oxidation of the corresponding alcohols, the aldehyde at the moment of formation uniting with the alcohol, and this tendency to combine is much increased if acetic acid is present (Geuther, Annalen, 126, 65), or if pure hydrogen phosphide is passed through the cooled mixture of aldehyde and

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[1] The b.p. is given as in the original paper, but, inasmuch as b.p. of acetal is 104°, it seems probable that 95° is a misprint for some higher temperature—say 105°.

alcohol (Girard, Compt. rend. 91, 629 ; J. 1880, 695).

They are formed readily by the interaction of aldehydes with very dilute alcoholic hydrochloric acid (Fischer and Giebe, Ber. 30, 3053 ; 31, 545). Ketonic and aldehydic acetals, both aliphatic and aromatic, are formed by the interaction of nascent orthoformic ester and the necessary ketone or aldehyde in the presence of hydrochloric acid (Claisen, Ber. 31, 1010 ; Annalen, 237, 269).

The acetals are liquids having aromatic odours, and are sparingly soluble in water, from which they can again be separated on addition of concentrated calcium chloride solution. They are readily soluble in alcohol and ether ; their vapours or their solutions in alcohol benzene or acetones slowly harden dry gelatin films (Beckmann and Scharfenberger, Chem. Zentr. 1896, ii. 930). When heated in a closed tube with glacial acetic acid, the corresponding aldehyde is obtained (Beilstein, Annalen, 112, 239). According to Bachmann (Annalen, 218, 45) the series of acetals can be descended by heating any member of the group with an alcohol containing a smaller number of carbon atoms than is present in its alcohol residue ; for example, diethylacetal and methyl alcohol yield dimethylacetal and ethyl alcohol ; but the reverse change, if it occurs at all, results in the production of very small quantities of the higher acetal. Delépine (Compt. rend. 1901, 132, 331, 968) finds, however, that when some acetals are boiled with any alcohol in the presence of a few drops of hydrochloric acid, a balanced reaction takes place. Thus whether methylal is heated with amyl alcohol or diamyl formal with methyl alcohol, the result is the same, the products consisting of a mixture of methylal, diamyl formal, methyl and amyl alcohols and the mixed acetal MeO·CH$_2$·OC$_5$H$_{11}$, the products of higher molecular weight predominating. Mixed acetals— that is, acetals containing two different alcohol residues—described by Bachmann (l.c.), consist of mixtures of molecular proportions of two distinct acetals (Rübencamp, Annalen, 225, 271 ; Fritsch and Schumacher, Annalen, 279, 308), but Delépine (l.c.) seems to have obtained such acetals and also their chloro- derivatives. The latter have also been obtained by Magnamini (Gazz. chim. ital. 16, 330).

The following acetals have been prepared : methylal, which is an excellent solvent for many organic compounds (Kane, Annalen, 19, 175 ; Brühl, Annalen, 203, 12) ; ethylidene-dimethyl (Arlsberg J. 1864, 485), -dipropyl, and -diisobutyl (Girard, J. 1880, 695), and -diisoamyl ether (Arlsberg, J. 1864, 486) ; propylidenedipropyl ether (Schudel, Monatsh. 5, 247) ; isobutylidenediethyl ether (Oeconomides, Bull. Soc. chim. 35, 500) ; and amylidene-dimethyl, -diethyl, and -diisoamyl ether (Arlsberg, l.c.). Glycolacetal, a derivative of glycolaldehyde, has also been prepared (Pinner, Ber. 5, 150 ; Varley, Chem. Zentr. 1899, ii. 919).

A large number of halogen alkyl and other acetal compounds have been prepared (Fischer, Ber. 26, 464 ; 41, 2860 ; 42, 1070 ; Fritsch (l.c.) ; Wolff, Ber. 21, 1481 ; Wohl, Ber. 21, 616 ; 22, 568, 1353 ; Wohl and Lange, Ber. 40, 4727 ; Heller, Löb, Alexander, Ber. 27, 3097, 3093, 3102 ; Fosse nd Etlinger, Compt. rend. 130,

1194 ; Delépine, l.c. and Compt. rend. 131, 748 Stollé, Ber. 35, 1590 ; Oddo and Mameli, Gazz chim. ital. 33, ii. 373 ; Atto, R. Acad. Lincé 1905, [v] 14, ii. 587 ; Freundler, Compt. rend 138, 289 ; Bull. Soc. chim. 1907, [iv] 1, 66 Tschitschibabin, J. pr. Chem. 1906, [ii.] 73 326 ; Paal and Gember, Arch. Pharm. 246, 306 Arbusoff, J. Russ. Phys. Chem. Soc. 40, 637 Smiles, Chem. Soc. Trans. 1909, 1000). Th mono- and di-acetal derivatives of catechol (pyro catechin) are obtained by heating the mono sodium derivative of catechol with monochlor acetal (Moreu, Compt. rend. 126, 1656).

ACETALDEHYDE v. ALDEHYDES.

ACETAMIDE C$_2$H$_5$NO, or CH$_3$·CONH$_2$.

(Hofmann, Ber. 15, 980; Schulze, J. pr. Chem [2] 27, 512 ; Keller, J. pr. Chem. [2] 31, 364 Aschan, Ber. 31, 2344 ; Kündig, Annalen, 105 277 ; Abel, J. Soc. Chem. Ind. 1899, 515. Acetamide is usually prepared by the dry distillation of ammonium acetate ; a better yield (91·7 p.c.) and a purer product is obtained by distilling ammonium diacetate in the special apparatus described by François (J. Pharm. Chim. 23, 230). Between 135° and 195° acetic acid and water are evolved, and at 195°-222° some acetamide passes over. When the temperature remains constant at 222° the distillation is stopped, the residue being pure acetamide. A nearly theoretical yield is obtained by saturating a mixture of ethyl acetate and ammonia with dry ammonia gas at ··10°, and after standing, fractionating in vacuo (Phelps, Amer. J. Sci. 24, 429).

Acetamide forms white hexagonal crystals which are odourless when pure, and melt at 81°-82° (Hofmann, Ber. 14, 2729 ; Mason, Chem. Soc. Trans. 1889, 107 ; Meyer, Ber. 22, 24 ; Forster, Chem. Soc. Trans. 1898, 791 ; Nicol, Zeitsch. anorg. Chem. 15, 397), boils at 222° (cor.) [Kündig], is readily soluble in water, and when heated with acids or alkalis is converted into acetic acid and ammonia (Coninck, Compt. rend. 124, 893 ; 126, 907 ; 127, 1028 ; Dunstan a. Dymond, Chem. Soc. Trans. 1894, 220 ; Guebet, Compt. rend. 129, 61). Chlorine, led into fused acetamide, yields acetchloramide CH$_3$·CONHCl; and bromine, in the presence of dilute aqueous potash or soda yields acetbromamide, which on distillation with concentrated aqueous soda is converted into methylamine (Hofmann, Ber. 15, 408); Buchner and Papendieck, Ber. 25, 1160; Selivanoff, Ber. 26, 423 ; François, Compt. rend. 147, 680 ; 148, 173 ; Behrend a. Schreiber, Annalen, 318, 371). Acetamide acts both as a base and an acid (Pinner and Klien, Ber. 10, 1896), combining with hydrogen chloride or nitric acid, and forming compounds in which a metal takes the place of one atom of hydrogen, as C$_2$H$_3$O·NHAg (Strecker, Annalen, 103, 321 ; Tafel and Enock, Ber. 23, 1550 ; Blacher, Ber. 28, 432 ; Hofmann and Bagge, Ber. 41, 312 ; Titherley, Chem. Soc. Trans. 1897, 467). According to Forster (Chem. Soc. Trans. 1898, 783), mercury acetamide is a powerful dehydrogenising agent and owing to its tendency to exchange its mercury for hydrogen when the latter is attached to nitrogen, particularly when hydroxyl groups are in proximity, it can be employed as a convenient means of detecting primary and secondary hydrazines and primary hydroxylamines. It has also a

marked tendency to form additive compounds (Morgan, Chem. Soc. Proc. 1906, 23). The hydrogen in the NH_2 group has also been replaced by alkyl groups (Titherley, Chem. Soc. Trans. 1901, 396, 411, 413). Acetamide forms molecular compounds of the type $CH_3 \cdot CONH_2, X$, where $X =$ an organic or inorganic acid or an inorganic salt (Titherley, *l.c.*; Topin, Ann. Chim. Phys. [7] 5, 99). When acetamide is treated with formaldehyde, paraldehyde, or trioxymethylene, condensation products of the type $R \cdot NH \cdot CH_2OH$ are obtained ; these products are of value as antiseptics and as solvents for uric acid (J. Soc. Chem. Ind. 1906, 283). Mono-, di-, and trichloracetamide (Willm, Annalen, 102, 110 ; Geuther, J. 1864, 317 ; Pinner and Fuchs, Ber. 10, 1066 ; Malaguti, Annalen, 56, 286 ; Cloëz, Annalen, 60, 261 ; Bauer, Annalen, 229, 165 ; Dootson, Chem. Soc. Trans. 1899, 171 ; Swartz, Chem. Zentr. 1899, [i.] 588 ; Clermont, Compt. rend. 133, 737). Bromo-dialkyl-acetamide (J. Soc. Chem. Ind. 1904, 1238) and other halogen derivatives have also been prepared (Selivanoff, J. Russ. Phys. Chem. Soc. 24, 132 ; Broche, J. pr. Chem. [2], 50, 97 ; Conrad, Ber. 29, 1042 ; Zinke and Kegel, Ber. 23, 230 ; Willstätter, Ber. 37, 1775 ; Steinkopf, Ber. 41, 3571 ; Swartz, *l.c.*; Francesconi, Gazz. chim. ital. 33, 226 ; Ratz, Monatsh. 1904, 25, 687 ; Einhorn, Annalen, 343, 203 ; Finger, J. pr. Chem. 1906, [ii.] 74, 153).

The acetamido β-naphthaquinones and some of their halogen derivatives which may be used in dyeing (Kehrmann and Zimmerli, Matis, and Locker, Ber. 31, 2405 ; Kehrmann and Aebi, Ber. 32, 932 ; Kehrmann and Wolff, Ber. 33, 1538) and other acetamide derivatives have been prepared (J. Soc. Chem. Ind. 1894, 60 ; Lumière, Bull. Soc. chim. 1903, iii. 30, 966 ; Ratz, Monatsh. 26, 1487 ; Miolati, Gazz. chim. ital. 23, 190).

Diacetamide $C_4H_7NO_2$, or $NH(C_2H_3O)_2$ and its derivatives (*see* Gautier, Z. 1869, 127 ; Hofmann, Ber. 14, 2731 ; Hentschel, Ber. 23, 2394 ; Curtius, Ber. 23, 3037 ; Mathews, Amer. Chem. J. 20, 648 ; König, J. pr. Chem. 1904, [ii.] 69, 1 ; Troeger, J. pr. Chem. 69, 347 ; *Triacetamide* $C_6H_9NO_3$, or $N(C_2H_3O)_3$ and its derivatives (*see* Wichelhaus, Ber. 3, 847).

ACETANILIDE $C_6H_5 \cdot NH \cdot CO \cdot CH_3$, also known as *Antifebrin*, is prepared by heating together glacial acetic acid and aniline for some time.

By substituting thioacetic acid for acetic acid the reaction proceeds more rapidly and at a lower temperature (Pawlewski, Ber. 1898, 661). Acetanilide may also be prepared by heating 1 part of aniline with 1¾ parts of dilute acetic acid or of crude pyroligneous acid under pressure at 150°–160° (Matheson & Co., Eng. Pat. 6220 and D. R. P. 98070 ; J. Soc. Chem. Ind. 1897, 559).

The substance melts at 114·2° (Reissert, Ber. 1890, 2243), at 115°–116° (Hantzsch and Fresse, Ber. 1894, 2529), and boils without decomposition at 303·8° (corr.) (Pictet and Crépieux, Ber. 1888, 1111), at 305° (corr.) (Perkin, Chem. Soc. Trans. 1896, 1216) ; it is soluble in hot water, alcohol, or ether.

Acetanilide is hydrolysed at 100° by caustic potash or by hydrochloric acid, but not by sulphuric acid (Hantzsch and Fresse, Ber. 1894, 2529) ; it is rapidly decomposed by chromic acid, liberating carbon dioxide, and producing

colouring matters (De Coninck, Compt. rend. 1899, 503). It reacts with zinc chloride at 180° with the formation of the yellow dye *flavaniline* (Braütigam, Pharm. Zeit. 44, 75).

Acetanilide is present in the urine of cows (Petermann, Ann. Chim. anal. 1901, 165). It is largely used in headache powders. For methods of estimation *v.* Puckner, Ph. Rev. 1905, 302, and Seidell, Amer. Chem. J. 1907, 1091. The following reactions may be used for detecting its presence : (1) bromine water added to a solution of acetanilide in acetic acid gives a white crystalline precipitate of *p*-bromacetanilide, m.p. 167° ; (2) evaporation of a solution to dryness with mercurous nitrate gives a green mass, changing to blood red on addition of a drop of concentrated sulphuric acid ; (3) ferric chloride gives no blood-red colouration with acetanilide, thus distinguishing it from phenacetin and antipyrine.

Derivatives.—Chloracetanilides (Jones and Orton, Chem. Soc. Trans. 1909, 1056) ; Nitroacetanilides (Holleman and Sluiter, Rec. trav. chim. 1906, 208).

ACETIC ACID. *Acide Acétique. Essigsäure. Acidum Aceticum.* $C_2H_4O_2$ *i.e.* $CH_3 \cdot COOH$, or $C_2H_3O \cdot OH$.

Acetic acid occurs in nature in the juices of many plants, especially trees, either as free acid or, generally, as the calcium or potassium salt ; and, in the form of organic acetates, in the oils from many seeds. It is stated to be present in larger quantities when the plants are kept from the light. It exists in certain animal fluids ; Béchamp states it to be a normal constituent of milk. Gmelin and Geiger have found it in mineral waters, doubtless from the decomposition of organic matter.

Being a very stable body both at the ordinary and at high temperatures, it is found as a product of the decomposition or destructive distillation of many organic substances. Acetic acid was first shown by Lavoisier to be formed by the oxidation of alcohol. Its true composition was ascertained by Berzelius in 1814, and Döbereiner in 1822 proved that it was formed, together with water, by the oxidation of alcohol, without the formation of carbonic acid as had been previously supposed.
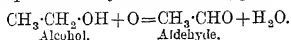
Preparation.—Acetic acid is produced by the oxidation, decomposition, and destructive distillation of many organic bodies. The greater part of that used in commerce is obtained by the destructive distillation of wood.

Alcohol may be converted into acetic acid by powerful oxidising agents, such as chromic acid, nitric acid, &c. Advantage may be taken of the fact that spongy platinum or platinum black has the property of absorbing oxygen, and thus acting as a powerful oxidising agent. If spongy platinum be placed over a vessel of alcohol with free access of air, the platinum absorbs at the same time the oxygen and the alcohol vapour, which combine and produce acetic acid and water :—

$$CH_3CH_2OH + O_2 = CH_3COOH + OH_2.$$
Alcohol.   Acetic acid.
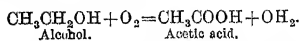
In addition to acetic acid, aldehyde (acetic aldehyde) is produced, which is intermediate in composition between alcohol and acetic acid. It is formed by the removal of two

atoms of hydrogen from the alcohol without their replacement by an atom of oxygen :—

$$CH_3 \cdot CH_2 \cdot OH + O = CH_3 \cdot CHO + H_2O.$$
Alcohol.   Aldehyde.

In presence of excess of oxygen aldehyde forms acetic acid. Aldehyde is a very volatile liquid, and is liable to be lost before its conversion into acetic acid ; it is therefore necessary in all cases where acetic acid is produced by the oxidation of alcohol to allow free access of air.

This method produces a very pure acetic acid, but on account of the initial cost of the platinum (which, however, is not in any way injured by use) it is not used on the manufacturing scale.

Patents have been taken out in England for the acetification of alcoholic liquors by ozone and by nascent oxygen and also for the manufacture of acetic acid from alkali acetates by electrolysis (Plater-Syberg, Eng. Pat. 1898, 233). A French patent (360, 249, 1905) describes the preparation of acetic acid from acetylene. Acetylene is passed into a solution of a normal mercuric salt which precipitates mercury acetylide. The liquid is then boiled, when aldehyde is formed and the mercuric salt reformed. The aldehyde is then oxidised to acetic acid.

Several kinds of ferments are capable of converting fermented alcoholic liquors into acetic acid. The two chief are the *Mycoderma aceti* of Pasteur, also known as *Mycoderma vini*, ' mother of vinegar ' and ' the vinegar plant,' and the *Bacterium xylinum* of Brown. Buchner and Meissenheimer have shown that the fermentation is due to enzymes in the plant-cell. They are white gelatinous nitrogenous plants, requiring for their healthy growth proteid substances and mineral salts, which are always present in wines and other alcoholic liquids. In the absence of this food they have no action on pure alcohol, but Pasteur has shown that pure alcohol, to which alkaline phosphate and ammonium phosphate have been added, is slowly acetified by this ferment, the ammonia supplying the nitrogen.

The *concentrated* or *glacial* acid is usually prepared by the distillation of a dry acetate with an equivalent quantity of strong sulphuric acid, or acid potassium or sodium sulphate.

Sodium acetate is generally used. The anhydrous salt is fused on sheet-iron pans, 6 feet by 4 feet, care being taken that no sparks reach the dried salt, as it would then ignite and burn like tinder. The mass is cooled, broken into small lumps, and distilled with concentrated sulphuric acid. The first portion distilling contains the water, the later portion is collected and cooled ; when crystals have formed the still liquid portion is removed, the crystals are melted and redistilled as before, producing the glacial acid.

When a solution of calcium chloride is mixed with a solution of calcium acetate, crystals of calcium aceto-chloride $CaC_2H_3O_2Cl, 5H_2O$ gradually separate. These crystals may be produced in comparative purity even when impure brown acetate of lime is used. To obtain acetic acid ordinary commercial or ' distilled ' acetate of lime is mixed with the proper proportion of calcium chloride, and the solution is concentrated by evaporation until it crystallises; the mother

liquor is poured from the crystals and concentrated until the production of a second crop of crystals ; this is repeated until about four crops have been produced. The crystals are dissolved in water, filtered through animal charcoal, mixed with about 10 p.c. of calcium chloride, and recrystallised. The crystals are distilled with a mixture of 1 part sulphuric acid of sp.gr. 1·84 and 2 parts water, and the acetic acid concentrated in the usual way. The glacial acid may also be prepared by the distillation of di- or acid-acetate of potash, which, when heated, decomposes into acetic acid and the normal acetate of potash. If ordinary acetic acid be heated with normal potassium acetate, the acid acetate is formed, and a weaker acid at first distils over : as the temperature rises, the diacetate begins to decompose, and the distillate increases in strength until the glacial acid passes over. When the temperature reaches 300° the distillate becomes coloured from the decomposition of the acid (Melsens, Annalen, 52, 274 ; Compt. rend. 19, 611).

Scott and Henderson (Eng. Pat. 1896, 6711) purify the crude acetates by boiling with sodium hypochlorite until the colour is nearly gone. The solution is then cooled and allowed to settle. The clear liquid is decanted and crystallised. The crystals are of great purity. Scott (Eng. Pat. 1897, 12952) has patented a process which dispenses with lime in the manufacture of acetic acid. He distils the crude acid at 106°, and fractionally condenses the vapours. The acid collects mainly in the first portions.

Crude acetates may be decomposed with H_2SO_4 or HCl, and the acetic acid distilled *in vacuo* (Thompson, J. Soc. Chem. Ind. 1896, 357); or crude acetic acid may be treated with oxygen under pressure, filtered through charcoal and distilled over pure sodium acetate (Schmidt, Eng. Pat. 1896, 25100).

Hochstetter (J. Soc. Chem. Ind. 1902, 1469) prepares pure acetic acid by heating pure sodium acetate with dry HCl at 120°.

'Aromatic vinegar' may be prepared by distilling crystallised diacetate of copper (distilled verdigris). The acetate is dried at 160° and heated in earthenware retorts, when the glacial acid distils over. The verdigris produces about half its weight of the acid. The pleasant odour of aromatic vinegar is largely due to acetone, which is always produced when acetates of heavy metals are distilled, but camphor and essential oils are frequently added to increase or modify the smell.

Acetic acid for pharmaceutical and medicinal purposes should not decolourise a solution of potassium permanganate. To remove the organic matter which would have that effect, the acid is distilled with potassium permanganate or dichromate.

Properties.—The strongest acid solidifies at 16·7° in tabular or prismatic glistening crystals. The glacial acid may be cooled to −10° without solidification, even when agitated, but on the addition of a crystal of the acid the whole solidifies and the temperature rises to 16·7°.

The specific gravity of the crystals at 15°/4° is 1·0607 (Mendeléeff, J. 1860, 7). They melt to a mobile colourless liquid of sp.gr. 1·0543 at 16°/4° (Petterson, J. pr. Chem. [2] 24, 301), 1·0495 at 20°/4° (Brühl) which boils at 118·5° at 760 mm.

(Perkin). The liquid is uninflammable, but the vapour burns with a blue flame producing water and carbonic acid. When passed through a red-hot tube only a small portion is decomposed, producing carbon, acetone, benzene, &c. The strong acid blackens when heated with concentrated sulphuric acid, evolving sulphurous and carbonic anhydrides.

Nitric and chromic acids have no action; for this reason acetic acid is frequently used as a solvent for organic substances such as hydrocarbons, which are to be subjected to the action of chromic acid. Chlorine under the influence of sunlight replaces a portion of the hydrogen, and produces *mono-*, *di-* and *trichloracetic acids.* Similarly, bromine produces *dibromacetic acid.* On the addition of water to the glacial acid heat is evolved and the density increases until 20 p.c. of water is present; from this strength to 23 p.c. of water the density remains stationary. Further dilution lowers the density, so that either dilution or concentration from this point will produce an acid of diminished density. An acid containing only 43 p.c. of acid has the same density as the glacial acid. This, together with the slight difference between the density of acetic acid and water, renders it impossible to determine, with any precision, the percentage of acid by means of the hydrometer.

No definite hydrates of acetic acid are known (De Coppet. Ann. Chim. Phys. [7] 16, 275; Colles, Chem. Soc. Trans. 1906, 1247).

The following table shows the density of aqueous acetic acid at 15° and 20° :—

DENSITY OF AQUEOUS ACETIC ACID (OUDEMANS).

p.c.	Density 15°	Density 20°	p.c.	Density 15°	Density 20°	p.c.	Density 15°	Density 20°
0	0·9992	0·9983	34	1·0459	1·0426	68	1·0725	1·0679
1	1·0007	0·9997	35	1·0470	1·0437	69	1·0729	1·0683
2	1·0022	1·0012	36	1·0481	1·0448	70	1·0733	1·0686
3	1·0037	1·0026	37	1·0492	1·0458	71	1·0737	1·0689
4	1·0052	1·0041	38	1·0502	1·0468	72	1·0740	1·0691
5	1·0067	1·0055	39	1·0513	1·0478	73	1·0742	1·0693
6	1·0083	1·0069	40	1·0523	1·0488	74	1·0744	1·0695
7	1·0098	1·0084	41	1·0533	1·0498	75	1·0746	1·0697
8	1·0113	1·0098	42	1·0543	1·0507	76	1·0747	1·0699
9	1·0127	1·0112	43	1·0552	1·0516	77	1·0748	1·0700
10	1·0142	1·0126	44	1·0562	1·0525	78	1·0748	1·0700
11	1·0157	1·0140	45	1·0571	1·0534	79	1·0748	1·0700
12	1·0171	1·0154	46	1·0580	1·0543	80	1·0748	1·0699
13	1·0185	1·0168	47	1·0589	1·0551	81	1·0747	1·0698
14	1·0200	1·0181	48	1·0598	1·0559	82	1·0746	1·0696
15	1·0214	1·0195	49	1·0607	1·0567	83	1·0744	1·0694
16	1·0228	1·0208	50	1·0615	1·0575	84	1·0742	1·0691
17	1·0242	1·0222	51	1·0623	1·0583	85	1·0739	1·0688
18	1·0256	1·0235	52	1·0631	1·0590	86	1·0736	1·0684
19	1·0270	1·0248	53	1·0638	1·0597	87	1·0731	1·0679
20	1·0284	1·0261	54	1·0646	1·0604	88	1·0726	1·0674
21	1·0298	1·0274	55	1·0653	1·0611	89	1·0720	1·0668
22	1·0311	1·0287	56	1·0660	1·0618	90	1·0713	1·0660
23	1·0324	1·0299	57	1·0666	1·0624	91	1·0705	1·0652
24	1·0337	1·0312	58	1·0673	1·0630	92	1·0696	1·0643
25	1·0350	1·0324	59	1·0679	1·0636	93	1·0686	1·0632
26	1·0363	1·0336	60	1·0685	1·0642	94	1·0674	1·0620
27	1·0375	1·0348	61	1·0691	1·0648	95	1·0660	1·0606
28	1·0388	1·0360	62	1·0697	1·0653	96	1·0644	1·0589
29	1·0400	1·0372	63	1·0702	1·0658	97	1·0625	1·0570
30	1·0412	1·0383	64	1·0707	1·0663	98	1·0604	1·0549
31	1·0424	1·0394	65	1·0712	1·0667	99	1·0580	1·0525
32	1·0436	1·0405	66	1·0717	1·0671	100	1·0553	1·0497
33	1·0447	1·0416	67	1·0721	1·0675			

The addition of a small quantity of water lowers the melting-point of the glacial acid considerably, as shown by the annexed table (p. 10) Dahms (Ann. Chim. Phys. [7] 18, 141).

Acetic acid is monobasic, but forms both acid and basic, as well as normal salts. It dissolves certain metallic oxides, as those of lead and copper, forming basic acetates.

It has a pungent sour taste, and when strong blisters the skin. The glacial acid has no action on litmus, but on addition of water becomes powerfully acid. It is not affected by the electric current, probably because a bad conductor, but when a little sulphuric acid is added the current decomposes it, producing, according to Renard (Ann. Chim. Phys. [5] 16, 289), carbon dioxide, carbon monoxide and oxygen. Alkaline acetates when electrolysed are decomposed into hydrogen and alkaline hydrate which

appear at the negative pole, and ethane and carbon dioxide at the positive pole.

Solidifying-point	Water to 100 parts real acetic acid	Solidifying-point	Water to 100 parts real acetic acid
°C.		°C.	
16·675	0	−3·94	16·38
16·50	0·05	−8·80	21·53
16·06	0·29	−12·80	24·56
14·54	1·15	−18·10	29·97
11·81	2·94	−17·90	30·87
7·21	6·53	−23·87	36·57
2·95	10·33	−24·90	37·52
2·46	10·74	−25·20	39·30
−2·90	15·80	−26·75	40

Acetic acid mixes with alcohol and ether in all proportions. It dissolves resins, gelatin, fibrin, albumen, essential oils, &c. Phosphorus and sulphur are somewhat soluble in the warm acid.

Acetic acid is largely used in the preparation of the acetates of copper, aluminium, iron, lead, &c.; as pyroligneous acid in calico printing; in the preparation of varnishes and colouring matters; in the laboratory and certain industries as a solvent; for domestic use; in photography; and in medicine as a local irritant and to allay fever, and in the form of smelling salts.

Analysis.—Commercial glacial acid should contain at least 97 p.c. of absolute acid. If 9 volumes oil of turpentine be agitated with 1 volume of acid, no turbidity will be produced if the acid contain 97 p.c. or upwards. Acid of 99·5 p.c. produces no turbidity with any proportion of turpentine (Bardy, Chem. News, 40, 78).

A very delicate test for the presence of water is to mix the acid with an equal bulk of carbon disulphide in a dry tube, and warm with the hand for a few minutes; in presence of a trace of water the liquid becomes turbid.

The commercial acid may contain sulphuric acid, sulphates, sulphurous acid, hydrochloric acid, chlorides, arsenic (derived from sulphuric acid), and copper, lead, zinc, and tin derived from the vessels used in the manufacture.

The presence of sulphuric acid or sulphates is shown by the production of a white precipitate with barium chloride. To the filtered solution bromine or chlorine water is added, producing, if sulphurous acid be present, a further precipitate of barium sulphate. Hydrochloric acid and chlorides are detected and estimated with silver nitrate.

In testing for metals a considerable bulk of the acid should be evaporated; a few drops of hydrochloric acid are added, and a current of sulphuretted hydrogen passed through the liquid; a black or brown colouration or precipitate indicates lead or copper. Copper may also be detected in the evaporated liquid by the brown precipitate produced on the addition of potassium ferrocyanide, and estimated by electro-deposition. To test for zinc, the solution, after the passage of sulphuretted hydrogen, is filtered, nearly neutralised with ammonia, and sodium acetate added, when zinc will be pre-

cipitated as white sulphide. For arsenic Reinsch's or the electrolytic test may be used.

Small quantities of acetic acid may be recognised by neutralising with caustic potash, adding arsenious oxide, evaporating to dryness, and heating, when the characteristic smell of cacodyl is evolved.

To determine the free acetic acid in a solution it is usual to titrate a weighed quantity with caustic soda standardised with acetic acid of known strength, or of acid potassium tartrate (Stillwell and Gladding).

As indicator litmus may be used, but as it is rendered blue by the normal sodium acetate, it is preferable to use phenol-phthalein, to which that substance is neutral; this is also more sensitive, and, where coloured, the liquid may be considerably diluted without impairing the delicacy of the reaction.

To estimate small percentages of water in acetic acid, the solidifying-point may be determined and the percentage found by the table before given.

For the separation and estimation of formic, acetic, propionic, and butyric acids see Zeit. Anal. Chem. 1899, 38, 217. Chapman (Analyst, 1899, 24, 114) describes a method for the estimation of *iso*valeric acid in acetic acid.

The acetic acid in acetates may be determined by distilling about 1 gram of the salt nearly to dryness with 10 c.c. of a 40 p.c. solution of phosphoric acid (free from nitric and other volatile acids); water is added and the distillation repeated to remove the last traces of acetic acid; the distillates are mixed and titrated as above with standard alkali. This method of distillation may also be used for highly coloured solutions of acetic acid where direct titration is inadmissible.

Preparation of Vinegar.

In all processes for the manufacture of vinegar advantage is taken of the oxidising action of the vinegar fungus already described; the souring of wines and other alcoholic liquids is due to this organism, the germs of which are always present in the air, and are deposited and grow in any suitable medium.

The action is more rapid when the liquid is rich in vegetable matter and poor in alcohol, and when the surface exposed to the air is large. The percentage of alcohol should not, however, be too low; the acetous fermentation proceeds but slowly in a liquid containing less than 3 p.c. alcohol.

Wine vinegar. (Fr. *Vinaigre*; Ger. *Weinessig*.) In the wine district of Orleans, wines which have become sour are generally used for the preparation of vinegar. For this purpose fullbodied wines are preferred. If they contain above 10 p.c. alcohol they are suitably diluted with weaker wines. The wine, before being fermented, is usually left for some time in contact with beech shavings, on which the lees are deposited, rendering the wine brighter. A certain amount of extractive matter is, however, necessary for the proper growth of the plant, and if the wine be old and the matter deposited, the fermentation is much retarded. Wine one year old is preferred.

The 'Vinaigrerie' is usually a building of southern aspect; the rooms in which the

process is conducted are low-roofed, and the walls are provided with openings for the admission of air, which can be closed when the temperature is not sufficiently high.

A number of casks of well-seasoned oak, bound with iron hoops, each holding from 50 to 100 gallons are supported on their sides in rows about 18 inches from the floor, one set being frequently placed above another, in which case those nearest the roof are found to work most rapidly. Each cask is bored with two holes in the front end, a larger one, the 'eye,' for the addition of wine or the removal of vinegar, and a small one for the admission of air.

When first used the casks are thoroughly scalded with boiling water to remove extractive matter, one-third filled with boiling strong vinegar, and allowed to stand for eight days; from that time wine is added in charges of about 10 pints every eight days until not more than two-thirds full; after a further interval of 14 days a portion, varying from 10 gallons to half the total bulk, is drawn off and the periodical addition of the wine continued. The temperature of the chambers should be about 25°, and is kept up when necessary with a stove. In order to ascertain if the fermentation is completed at the end of the usual time, the workman plunges a white spatula into the liquid; if a reddish froth adheres, more wine is added and the temperature raised; a white froth indicates the completion of the process. More than eight days is sometimes required to complete the oxidation, in which case stronger wine and a higher temperature may be used. The sluggishness may, however, be due to the casks becoming foul, which occurs usually after about six years' working. The deposit of argol, yeast sediment, &c., is thoroughly removed, the casks cleansed and recharged with hot vinegar as in the case of new casks. Good casks will often last twenty-five years.

When working satisfactorily each cask will produce about twice its capacity of vinegar annually.

Before storing, the vinegar is usually passed through the 'rapes' where it is 'brightened' and the acetification completed.

In other parts of France and in Holland and on the Rhine the following method is used. The wine is placed in two large upright tuns about 9 feet high and 4 feet wide, open to the air. Each tun has a perforated false bottom about 12 inches above the true bottom; on this is placed a quantity of vine cuttings, stalks, &c., so as to expose a large surface for the formation of the fungus. One of the vats is half, and the other completely, filled. The acetification progresses more rapidly in the former; this, after twenty-four hours, is filled from the full cask, in which the action then increases. This alternate transference is continued daily until the acetification is complete. The most favourable temperature is about 24°. The vinegar is run off into casks containing chips of birch wood on which the lees settle, and in about fourteen days being thus clarified is stored in close casks for the market.

Malt vinegar. *Malzgetreide Bieressig. Acetum Britannicum.* This is prepared from an infusion of malt which has first been fermented to produce alcohol. Six bushels of crushed malt are extracted three times with water, in a circular mash tun supplied with a central stirrer, the first extraction with water at 72°, the second at a higher temperature, and the third with boiling water. The extracts, which together should not exceed 100 gallons, are passed into a large cast-iron tank 24 feet by 8 feet, cooled by refrigerators to 24°, poured into a large circular vessel, mixed with 3 or 4 gallons of good yeast and fermented briskly for about forty hours. The extract is filtered, and, where intended for the manufacture of the best keeping vinegar, is stored in casks for some months, whereby the extractive matters which would induce putrefaction are deposited.

This 'wash' may be treated by the 'quick vinegar process' or acetified in large casks lying on their sides in a room at a temperature of about 24°. The bung-holes of the casks are open, and at each end near the top an opening is made for the circulation of air. When conducted in the open air the process is known as 'fielding'; from eight to twenty rows of casks constitute a vinegar field. The operation is commenced in the spring and completed in about three months.

The fermenting casks are frequently worked in pairs; one being completely and the other three parts filled, acetification progresses more rapidly in the latter; every day a portion is transferred thereto from the full cask, being replaced by an equal amount of the more fermented liquid, until completed.

Before storing, it is necessary to filter the vinegar from the extractive matter. The filtering vessel, 'rape' or 'fining tun,' is a large cask, usually wider at the base than at the top, fitted with a false bottom, above which it is filled with spent tanner's wood, wood shavings, or, which is far preferable, with 'rapes,' the pressed cake of residue from the British wine manufacture, consisting of the stalks and skins of grapes and raisins. Through this the vinegar is poured, escaping through a tap beneath the false bottom into a tank from which it is continuously pumped to the top of the vessel and again passed through until the last traces of alcohol have been oxidised and the vinegar cleared and brightened. In this way pickling vinegar is produced.

For household vinegar, the malt is acetified in upright casks fitted with false perforated bottoms covered with a layer of rapes; after twenty-four hours it is transferred to another similar cask, remaining there for two or three days, and thence to a third and fourth cask. A portion of the liquid is transferred to the 'mothers' and the remainder allowed to ferment. A little argol is occasionally added to produce a flavour of wine vinegar, the liquid being clarified with isinglass.

Vinegar casks are made in three sizes, holding 25, 50, and 116 gallons.

Quick vinegar process. *Schnellessigbereitung.* This method, applicable to any alcoholic liquid, is founded on that proposed in 1720 by Boerhaave, and was first introduced by Schutzenbach in 1823. It differs from the other processes in causing the liquid to expose a very large surface to the action of the air, one gallon being sometimes made to cover a surface of 100 square yards.

The vat is usually from 6 to 12 feet high, and from 3 to 4 feet wide. In England it is frequently as much as 13 feet high, 14 feet wide at the top, and 15 feet wide at the base. At a distance of 18 inches from the bottom, six or more air holes are bored 1 inch in diameter, inclining downwards towards the inside; just above these a false perforated bottom is fixed. A quantity of beechwood shavings is thoroughly washed with hot water, dried and placed on the false bottom, nearly filling the vat. The shavings may be substituted with advantage by pieces of charcoal about the size of a walnut, from which the saline particles have been removed by acid and subsequent washing. The acetifying action is assisted by the power of absorbing oxygen possessed by the charcoal.

Near the top of the tun is fixed a wooden disc perforated by holes as large as a quill, about 1 inch apart; through these, twists of cotton yarn or string are passed, of sufficient length to touch the shavings: they are tied into knots at the upper end to prevent them from slipping through. There are also five or six larger holes through which pass glass draught tubes projecting on either side of the disc, 1 to $2\frac{1}{4}$ inches wide and 4 to 6 inches long, firmly fastened so that no liquid can pass round them through the hole.

About 1 inch from the true bottom is fixed a bent tube attached to a tap through which the vinegar is drawn as soon as it rises to a height of about 15 inches. The vessel is closed with a tightly-fitting lid through which a circular opening is cut for the admission of liquid and for the escape of air.

Before commencing the fermentation it is necessary to ' sour ' the shavings; for this purpose hot vinegar is poured in from the top and allowed to soak for at least twenty-four hours.

The composition of the fluid used varies considerably: any alcoholic liquid may be used, but the presence of a trace of tarry matter, such as is present in pyroligneous acid, prevents the action. According to Wagner (Chem. Technology), the following mixture is generally used: —$4\frac{1}{2}$ gals. (20 litres) brandy of 50°Tralles (42·5 p.c. by weight), 9 gals. vinegar, and 27 gals. water, to which is added a mixture of bran and rye to promote the growth of the vinegar fungus.

Another standard liquor is 50 gals. brandy or whisky 52 p.c. by weight, 37 gals. beer or malt wort with about $\frac{1}{1000}$ part of ferment; this is mixed with 3 to 4 vols. of soft water before passing through the tuns. Molasses or honey in the proportion of 2 lbs. to 50 gals. is sometimes added, to produce a more finely coloured vinegar.

For ' wine malt,' 40 lbs. wheat-meal and 80 lbs. barley-meal are ground, and mixed together with 40 gals. warm water (50°); after settling, the clear liquid is drawn off, the residues are treated with hotter water (70°), settled, the liquid removed and the residue again treated, this time with boiling or nearly boiling water, in such quantity that the total washings amount to about 100 gals. The solution is cooled, mixed with 15 lbs. yeast, and allowed to ferment at 27° for five or six days; it is then known as the ' gyle.' The temperature of the chamber being about 38° the liquid which, where the ' generator ' or ' graduator ' is new, is heated to 50°, or, where in use for some time and thus in good condition, to 25°, is poured over the

upper disc and trickles slowly down the twisted threads, which swell and prevent too rapid passage. As the liquid flows over the shavings it becomes oxidised, the action being more rapid when, after some time in use, the shavings have become coated with the ' mother of vinegar.' When the action is satisfactory the temperature of the interior rises on account of the oxidation to 37°, and creates a constant upward current of air which passes from the openings below the false bottom, round the shavings and through the tubes in the upper disc.

When the liquid contains no more than 4 p.c. alcohol, the vinegar which collects is entirely acetified, but where a stronger liquid is used it may be necessary to pass it three or four times through the graduator. When a strong vinegar is required, that produced from one of the above-mentioned liquids is mixed with a more alcoholic liquid, and again passed through, and this may be repeated until 1 oz. of the liquid will neutralise sixty grains pure dry potassium carbonate, corresponding to about 12 p.c. acetic acid by weight. Each graduator will contain about 80 gals. of liquid and will produce daily 15 gals. of good vinegar. One workman usually attends to ten tuns.

By this process, on account of the large surface exposed, a considerable loss of acetic acid, and hence of acetic acid, is unavoidable, amounting when properly carried out to about 6 p.c. of the whole; but if the temperature has been allowed to rise too high, the loss is greatly increased. At the same time sufficient air must be introduced to convert the alcohol directly into acetic acid, or the loss will be further increased by the formation of the volatile aldehyde.

By some makers the vapours from the tuns are passed over or through water to absorb the alcohol and aldehyde. For this purpose two floating gasometers are sometimes used: one rises and removes the air which has performed its work, while the other falls, keeping up a constant current of air through the generator. As each gas-holder falls it discharges the air through a cistern of water, which absorbs the volatile products and is used for the preparation of a further quantity of malt extract.

Recent improvements in the quick vinegar process have taken the form of labour-saving contrivances and of devices to avoid loss by evaporation. Leaker has patented a process whereby the acetification takes place in closed rectangular vessels containing shelves of absorbent woven material. To the vessel is attached a condensing worm into which the vapours are drawn by a fan.

About one-third of the total extractive matter in the malt is lost or dissipated in the fermentation and acetification.

In Singer's generator a number of vessels are placed one above another in a shed in which a suitable temperature is maintained and from which draughts are excluded. The vessels are connected together by wooden tubes provided with longitudinal slits through which air can pass. The liquid slowly drops through the tubes from one vessel to another, and, exposing a large surface to the air, becomes acetified. It is stated that the loss of alcohol usually experienced is avoided in this process. In many vinegar works the larvæ of the ' vinegar fly '

(*Drosophila cellaris*) and ' vinegar eels ' (*Anguillula aceti*) abound.

Vinegar is found occasionally to decompose when shaken, probably on account of the lees becoming mixed with the liquid.

Of late years delicacy and uniformity of flavour in the various kinds of vinegars have been obtained by the use in acetification of pure cultures of the particular bacterium (Henneberg, Zeit. für Spiritusind. 1898, 180, and Cent. Bakt. 1905, 14, 681; Rothenbach, Woch. für Brau. 15, 445, and Deut. Essiggind, 1905, 9,217, and Woch. für Brau. 1906, 23, 260; Mayer, Zeit. für Spiritusind, 21, 334; Büchner and Gaunt, Annalen, 1906, 349, 140).

In addition to wine and malt, vinegar is prepared from many other substances. *Cider vinegar* is of a yellowish colour, sp.gr. 1·013 to 1·015. It contains 3½ to 6 p.c. acetic acid, and on evaporation leaves a mucilaginous residue, smelling and tasting of baked apples, and containing malic but not tartaric acid. The residue varies from 1·5 to 1·8 p.c. Genuine cider vinegar is distinguished from spurious cider vinegar by the residue, which consists of glycerol, albuminous matters, gums, malic and other organic acids and mineral matters. They have no rotation and little cupric reducing power after the usual clarification with basic lead acetate solution. The ash of a pure cider vinegar amounts to not less than 0·25 p.c., consisting mainly of potash, with small quantities of alumina, lime, magnesia, sulphate, and phosphate, variable amounts of carbonate, and complete absence of soda. Spurious cider vinegars have a molasses-like residue and an ash with a large percentage of lime or soda (Doolittle and Hess. *See* also Smith, J. Amer. Chem. Soc. 1898, 20, 3; Leach and Lythgoe, *l.c.* 1904, 26, 375; Van Slyke, New York Agric. Exp. Stn. Bull. 1904, 258, 439; Ladd, N. Dakota Exp. Stn. Bull. 32, 278). *Perry* and *crab-apple vinegars* are used in Wales and Monmouthshire, and possess characteristic properties.

Ale vinegar is prepared from sour strong pale ale. It usually gives a large residue (5 to 6 p.c.), and is very liable to decomposition. *Crystal vinegar* is ordinary vinegar decolourised by filtration through animal charcoal. A household vinegar is made in Germany from 7½ gals. soft water, 2 lbs. honey or brown sugar, 1 gal. whisky or corn spirit, 2 ozs. cream of tartar.

Glucose or *sugar vinegar* is prepared by the conversion of amylaceous substances into sugar, by the action of dilute acids, followed by fermentation and acetification. It contains glucose, dextrin, and very often gypsum, with hardly any proteins. The ash is composed mainly of potassium salts, is rich in sulphates, and in the case of cane-sugar vinegars, readily fusible (Allen's Comm. Org. Anal. 1909, 498). It is stated to be used for adulterating wine vinegar. It can be distinguished from other vinegars by the addition of 3 or 4 volumes strong alcohol, which produces a slimy precipitate of dextrin. Barium chloride usually gives a copious precipitate, due to the sulphuric acid used in the manufacture of the glucose.

Vinegar is now made from skim milk by addition of sugar, neutralisation with chalk, pitching first with yeast and then with *Mycoderma aceti* (Barbier Fr. Pat. 1903, 334071).

An artificial vinegar is made by mixing acetic acid with water and adding burnt sugar (caramel) and acetic ester to produce the proper colour, odour, and taste. This vinegar differs from genuine kinds by the absence in the evaporated residue of phosphoric, tartaric, or malic acid.

Properties.—Malt vinegar is a brown liquid of a characteristic odour due to the presence, in addition to the acetic acid, of acetic and other esters. Acetic ester is frequently added in small quantity to increase this aroma.

The vinegar of the B.P. has a sp.gr. of 1·017 to 1·019. In commerce it usually occurs in four strengths, numbered 18, 20, 22, and 24. The last is ' proof ' vinegar; it contains 6 p.c. acetic acid, and its sp.gr. is 1·019. The numbers denote the fact that one fluid ounce of the liquid will neutralise 18, 20, 22, and 24 grains respectively of pure dry sodium carbonate. The real weight of acetic acid in one ounce of liquid may be found by multiplying its number by 1·132, and the percentage by weight by multiplying the number by 0·259. Thus No. 24 should contain 6·22 p.c. of absolute acetic acid.

The addition of 1 part sulphuric acid to 1000 parts vinegar is lawful, and is occasionally made, though the idea that it prevents decomposition has been shown to be erroneous.

Malt vinegar usually contains alcohol, gum, sugar, and extractive matter, acetates, chlorides, free and combined sulphuric acid, and on evaporation and ignition leaves a residue containing much phosphate.

Wine vinegar varies in colour from pale yellow to red; that made from white wine is most esteemed; it usually has an alcoholic odour. Its sp.gr. is 1·014 to 1·022; it contains from 6 to 12 p.c. acetic acid. A litre (1·76 pint) of Orleans vinegar usually saturates 6 or 7 grams (92 to 108 grains) of pure dry sodium carbonate. On evaporation the total extract varies from 1·7 to 2·4 p.c., of which 0·25 p.c. is usually potassium tartrate, a salt peculiar to wine vinegar. The residue, with the exception of the tartar, should dissolve in alcohol.

The proof vinegars of various countries differ considerably; the minimum of acetic acid allowed by the various Pharmacopœias is—France, 8 to 9 p.c.; England, Germany, and Austria, 6 p.c.; Belgium, 5·6 p.c.; Russia, 5 p.c.; United States, 4·6 p.c. Genuine vinegar seldom falls below 5 p.c., and should be condemned as adulterated with water when the amount is as low as 3 p.c.

Analysis of Vinegar.

The adulterants to be looked for in vinegar are mineral acids, especially sulphuric acid, more rarely hydrochloric, and still more rarely nitric acid, tartaric acid, and pyroligneous acid; flavouring agents, cayenne, ginger, &c.; metals —usually derived from the vessels used—copper, lead, zinc, tin, arsenic (from sulphuric acid).

The presence of free mineral acids may be detected by the addition of Paris violet (methylaniline violet). Prepare a solution of this dye by dissolving 1 part in 1000 parts water, and add two or three drops of the solution to about one ounce of the vinegar. In presence of 1 p.c. free mineral acid the colour is green, with 0·5 p.c. bluish-green, and with 0·2 p.c. blue (Hilger, Arch. Pharm. 1876, 193).

If mineral acids are added to vinegar in small quantity they liberate an equivalent amount of acetic acid from the acetates, until the acetates are wholly decomposed, and form salts with the base, thus ceasing to exist as free acids. As acetates on ignition produce carbonates, the presence of an alkaline reaction in the ash indicates the presence of acetates in the vinegar, and therefore the absence of free mineral acids, though these may have been added in small quantities in the first instance. If, however, the ash be neutral, the presence of mineral acids is indicated. Hydrochloric acid may be tested for by adding silver nitrate to the distillate from the vinegar.

Heavy metals may be considered absent if no darkening is produced on passing sulphuretted hydrogen for some time through the solution. To determine the acetic acid in vinegar 110 c.c. may be distilled until 100 c.c. have passed over. The 100 c.c. will contain four-fifths of the total acid, and may be titrated with standard alkali and phenolphthaleïn, making an allowance for the one-fifth left in the retort.

Formic acid may be estimated by the method recommended by Ost and Klein (Chem. Zeit. 1908, 32, 815). The acid is neutralised with alkali and titrated with permanganate. Other substances which reduce permanganate must be absent.

Oxalic acid may be estimated by concentrating the vinegar and then boiling with calcium acetate solution.

Potassium hydrogen tartrate is estimated by titration against $N/2$ alkali, and tartaric acid by conversion to potassium hydrogen tartrate and subsequent titration (Zeitsch. anal. Chem. 1908, 47, 57).

(For the estimation of methyl alcohol in vinegar, *see* Ann. Chim. anal. 1901, 6, 127 and 171.)

Cayenne pepper, ginger, and other flavouring matters may be discovered by neutralising the vinegar and tasting.

Chevallier has found fuchsine in French wine vinegars.

Metallic Acetates.

Aluminium acetates.

The triacetate or normal acetate $Al_3(C_2H_3O_2)_6$ is not known. A solution corresponding to this compound, but which appears to be a mixture of the diacetate and acetic acid, is the only acetate of commercial importance. It is known as ' red liquor ' or ' mordant rouge,' and is largely used in dyeing and calico-printing, especially for the production of red colours, madder reds and pinks (whence its name of red liquor) ; for the production of dense lakes, and for waterproofing woollen fabrics. It is prepared by several methods.

A solution of alum is added to acetate of lime liquor. The lime is precipitated as sulphate, its place being taken by the aluminium forming aluminium acetate ; sulphate of ammonia or potash (according to whether ammonia or potash alum has been used) is produced at the same time. The mixture is agitated and allowed to settle, and a small quantity of the clear fluid removed and tested by the addition of alum ; if a precipitate forms sufficient alum has not been used and more must be added. The solution is filtered and concentrated to a specific gravity of 1·087 to 1·10 and allowed

to deposit any sulphate of lime still present. Sulphate of lime, being slightly soluble in water, is contained in the liquid in small quantity, and diminishes the brilliancy of the colours produced. By the substitution of lead acetate for the calcium acetate a better product is obtained. For this purpose 100 lbs. alum is dissolved in 50 gallons water, and treated with 100 lbs. finely-powdered lead acetate with constant stirring : or, using the same quantities, 10 lbs. crystallised carbonate of soda is added before the acetate of lead ; or, to 100 lbs. alum in 50 gallons water 6 lbs. of carbonate are added in small portions followed by 50 lbs. of lead acetate. The addition of the carbonate is made with a view to the production of a basic sulphate of alumina as well as the acetate, and as the sulphate assists the mordanting, less acetate is required. The solutions are allowed to settle and decanted. They contain the aluminium acetate mixed with basic aluminium sulphate and alkaline sulphate.

An aluminium sulpho-acetate appears to act satisfactorily. It is prepared by mixing (1) 453 lbs. ammonia alum (or 383 lbs. aluminium sulphate), 379 lbs. lead acetate, 1132 lbs. water ; or (2) 453 lbs. alum (or 333 lbs. aluminium sulphate) and 158 lbs. acetate of lime. The mixture is agitated, settled, and the clear liquid decanted.

By the use of aluminium sulphate, red liquor of the same density contains much more of the active alumina than that prepared with alum. Thus in a sample of the former 1 gallon contained 4 oz. 416 grs. alumina whilst the average amount found in three samples prepared from alum was 3 oz. 245 grs. The addition of a little ammonia or other alkali to the red liquor prepared from aluminium sulphate is advantageous for certain colours. Red liquor usually contains from 3 to 5 p.c. alumina (Al_2O_3) and 6 to 10 p.c. acetic acid ; its density varies from 1·085 to 1·120.

Ammonium acetate $C_2H_3O_2NH_4$.

The crystalline salt is usually prepared by saturating glacial acetic acid with dry ammonia gas. In solution it may be prepared more cheaply by neutralising acetic acid solution with ammonia. On evaporation, a solution of the salt loses ammonia, and leaves the acid acetate or diacetate.

Ordinary solid ammonium acetate always has an odour of acetic acid ; it is very soluble in water and alcohol.

Pure ammonium acetate should be entirely volatilised on heating. The commercial salt usually contains the same impurities as sodium acetate.

Calcium acetate. *Diacetate of lime. Pyrolignite of lime.* $Ca(C_2H_3O_2)_2$.

This important salt is prepared by neutralising acetic acid, or pyroligneous acid, with lime or chalk.

In the preparation from pyroligneous acid, the crude acid may be used, in which case the acetate of lime is known as *brown acetate* ; or the distilled liquor may be employed, producing *grey acetate*. The acid is placed in large wooden or iron pans, and powdered chalk or lime added in slight excess ; the liquor remains at rest at a warm temperature until settled, and is then siphoned off into the evaporating pans. It is generally evaporated by coils of pipe through

which steam passes; in this case the vessels are usually wooden, and lined with lead, but sometimes iron pans are used, the evaporation being conducted over a fire. As the liquid evaporates, tarry impurities rise to the surface, and are removed with a skimmer. As the acetate forms, it is withdrawn and drained in wicker baskets suspended over the pans.

The proper drying of the salt is necessary to the formation of a good product. In large works a drying house is used, which is usually a wind furnace 7 or 8 feet long, $4\frac{1}{2}$ feet broad. It is first heated from $75°$ to $115°$, and the fire slackened; the salt is then spread over the bottom to the depth of about 2 inches, and when somewhat dry an equal quantity is spread above it, the salt is repeatedly turned, and the heat continued for about 24 hours. When apparently dry, the heat is increased to about $125°$, and the last traces of moisture driven off. Care must be taken that the heat is not too high, or the salt becomes decomposed. As in the case of sodium acetate, no sparks must touch the mass, or it may burn away like tinder.

The product, when prepared from the *brown* liquor, is dark-coloured and contains charcoal and decomposed tarry matters; it may be dissolved in 3 parts hot water, filtered through animal charcoal, and again evaporated and crystallised yielding a nearly colourless product.

Pure calcium acetate crystallises in silky needles or prisms containing two molecules of water. At the ordinary temperature the crystals effloresce, and at $100°$ become anhydrous, forming a white powder of saline taste, very soluble in water.

Calcium acetate is used in the preparation of other acetates, and of acetic acid, and in calico-printing. The pure salt is completely soluble in water and proof spirit. The commercial article usually contains 62 to 67 p.c. of real acetate, and 1 to 8 p.c. of matters insoluble in water. The impurities are hydrate, carbonate, and sulphate of lime and tarry matters; formate and other salts of lime with fatty acids also occur.

Many methods of assay for this substance are in use, varying considerably in accuracy.

The most trustworthy method is to distil with pure phosphoric acid and titrate the distillate as already described under acetic acid (*see* Stillwell, J. Soc. Chem. Ind. 1904, 305; Grosvenor, *ibid.* 530; Gladding, J. Ind. Eng. Chem. 1909, 250).

Calcium aceto-chloride $CaC_2H_3O_2Cl,5H_2O$ has already been described as used in Condy's process for the preparation of pure acetic acid.

Copper acetates.

The normal *copper acetate* is prepared by dissolving cupric oxide or verdigris in acetic acid; or by the action of copper sulphate on the acetates of lead, calcium, or barium.

It crystallises in prisms; soluble in 13 parts cold or 5 parts hot water, and in 14 parts alcohol. In commerce it usually occurs in bunches of deep-green coloured opaque crystals known as 'grappes.'

Copper acetate is used in the manufacture of pigments; as an oxidising agent in the indigo vat; and; to a slight extent, for the preparation of acetic acid.

Basic copper acetate. *Verdigris. Vert-de-gris. Vert. de Montpellier. Grünspan.*

This substance consists of a mixture of mono-, di-, and tri-basic acetates of copper, which are present in different proportions in different varieties of verdigris.

At Grenoble and Montpellier the following process is used: The ' marcs ' or residues from the wine factories, consisting of the skins and stems of grapes, are loosely placed in earthen vessels, about 16 inches high, 14 inches in diameter at the widest part, and 12 inches at the mouth, covered and allowed to ferment, until on inserting a piece of copper (previously moistened with verdigris and dried), it becomes uniformly coated green in 24 hours. The fermentation should not proceed too far, or decomposition may ensue.

The copper used is in sheets $\frac{1}{24}$ inch thick, 4 to 6 inches long, and 3 to 4 broad, each weighing about 4 oz.; they are freed from scales, if necessary, rubbed with a solution of verdigris and dried; unless this precaution be adopted, the first coating produced by the marcs will be black instead of green. They are heated over a charcoal fire until as hot as the hand can bear, and placed in an earthenware vessel in layers with the marcs. 30 to 40 lbs. of copper are used for each vessel. In from ten to twenty days, according to the temperature, the covers are removed, when, if the process has progressed favourably, the marcs will be whitish and the copper covered with fine, glossy, green crystals. The plates are then removed and placed on end one against another. After two or three days they are moistened by immersion in water or damaged wine, and again placed on end for about a week. This alternate moistening and exposure to the air is continued for about six or eight weeks. The plates thus become covered with increasing coatings of the verdigris, which is detached and the plates are again used until entirely eaten away. The verdigris is kneaded with a little water into leather bags, pressed into rectangular cakes and dried.

This substance is known as *blue verdigris*, and consists principally of the basic acetate

$$(C_2H_3O_2)_2Cu_2O.$$
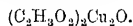
It should be dry, of a fine bluish colour, and soluble in dilute acids and ammonia.

Green verdigris contains as a principal constituent the sesquibasic acetate, $CuO\cdot2Cu(C_2H_3O_2)_2$, and is prepared by placing the copper plates alternately with cloths moistened every two or three days with pyroligneous acid or acetic acid until the plates show green crystals. The plates are arranged so as to allow free access of air and occasionally moistened, for five or six weeks. Large quantities of verdigris are manufactured in England by this process from pyroligneous acid. The imports of verdigris are very small.

The various forms of verdigris are used as oil and water colours. With white lead it is used in Russia and Holland as an oil paint, which by double decomposition produces a peculiar green. The paint is considered a good preservative. Verdigris is used in dyeing and calico-printing, and for the preparation of Schweinfurth green and other copper paints.

Verdigris is frequently adulterated with chalk, sand, clay, pumice, and sulphates of copper, barium, and calcium. When brass sheets have

been used in the preparation instead of copper, zinc will also be present.

When warmed with dilute hydrochloric acid the sand, clay, baryta, &c., will remain undissolved, and may be weighed. The total residue in a good sample will usually amount to 3 p.c., but should not exceed 6 p.c.

Aceto-arsenite of copper. *Schweinfurth green* (v. ARSENIC).

Ferric acetate $Fe.(C_2H_3O_2)_3$. This salt is prepared by the addition of calcium or lead acetate to ferric sulphate or iron alum, avoiding excess of the acetate. It is used as a mordant, its action corresponding with that of aluminium acetate. An alcoholic solution is used in medicine.

For many purposes a mixture of ferrous and ferric acetates is preferred. It is prepared by repeatedly pouring pyroligneous acid on iron turnings until saturated with iron. The liquid is known at ' pyrolignite of iron,' ' bouillon noir,' ' liqueur de ferraille.'

Ferrous acetate $Fe(C_2H_3O_2)_2$. *Pyrolignite of iron ; iron liquor or black liquor.* Is prepared on the large scale by the action of crude pyroligneous acid of sp.gr. 1·035 to 1·040 on iron turnings, nails, &c., at a temperature of 65°. The solution is frequently agitated and the tarry matters skimmed from the surface as they rise.

It is found that the purified acid produces a less satisfactory liquor, a fact due, according to Moyret (J. Soc. Dyers, i. 117), to the presence of a small quantity of pyrocatechol in the crude acid, which forms a compound with the ferrosoferric oxide in the solution, and causes its intense colour and keeping properties.

The liquid is intensely black, of sp.gr. 1·085 to 1·090, and is evaporated until its density rises to 1·120, or sometimes to 1·140. It is then ready for use, and is known as ' printer's iron liquor.' The liquor of density 1·120 contains about 10 p.c. iron.

The density of the liquor used by dyers is frequently raised by the addition of copperas (ferrous sulphate) ; thus, the addition to 1 gallon of black liquor, sp.gr. 1·085, of ½ lb. copperas, would raise its density to 1·111. Tannin also is sometimes added.

Black liquor is also prepared by the action of ferrous sulphate on acetate of lime ; the liquor produced has an average density of 1·11, and always contains sulphate of lime. By the action of lead acetate on ferrous carbonate, carbonate of lead and ferrous acetate are produced.

Black liquor absorbs oxygen from the air, forming ferric acetate, which is always present in the liquid. To diminish this action clean metallic iron is frequently added.

It is largely used in calico-printing and in dyeing, in the preparation of blue, violet, black, brown, and other colours, and for producing a black colour on hats, furs, leather, wood, &c.

Lead acetate. *Normal or di-acetate of lead. Sugar of lead. Sel de Saturne. Bleizucker.* $Pb(C_2H_3O_2)_2$.

For the preparation of *white acetate* of lead, leaden vessels are used, or copper pans, on the bottom of each of which a piece of metallic lead is soldered to produce a galvanic action and prevent the copper from being acted upon. In the vessel acetic acid of 45 p.c. or less is placed, and to 100 parts of 45 p.c., or a proportionate

quantity of a weaker acid, 86·5 parts of litharge are added in small quantities, with constant stirring, until the liquid is nearly neutral ; it is then heated to boiling and impurities skimmed from the surface, transferred to another vessel and evaporated to a density of 1·5, and removed to the crystallising pans, which are usually of wood, lined with lead or copper, 4 feet by 2 feet, and 6 or 8 inches high. The coarsely crystalline mass thus obtained is drained on wooden racks, and broken into lumps for the market.

A coarser variety, known as *brown acetate*, is prepared by substituting distilled pyroligneous acid for the purer acid. The muddy liquid produced is settled in a large tun, and the supernatant liquid transferred to a large iron pan and heated to boiling. It is again allowed to settle, transferred to another pan, evaporated until crystallisation commences, and about 3 volumes of water added, causing the remaining impurities to rise to the surface. The liquid is skimmed and diluted if the liquid is not sufficiently clear, and again evaporated until a small portion of the liquid crystallises on removing and cooling. It is then ladled into pans and allowed to crystallise.

As a rule, about 3 parts acetate are produced from 2 parts litharge.

By another method granulated lead, white lead residues, &c., are placed in vessels standing obliquely one above another ; the upper vessel is filled with strong acetic acid, which after the expiration of half an hour is allowed to run into the second vessel. Every half-hour it is removed to a lower one. After the acid has been removed, the lead absorbs oxygen rapidly, and becomes heated. On leaving the last vessel, the acid is again passed through the series, dissolving the acetate which has been formed, and is evaporated and crystallised.

Schmidt (Eng. Pat. 1897, 7192) describes a process for preparing the neutral and basic acetates of metals such as lead and copper by the action of dilute acetic acid and oxygen upon the metal contained in closed iron cylinders.

Pure lead acetate is a white crystalline salt of sweetish taste and weak acid reaction, containing 3 molecules of water. It dissolves in 1·5 parts cold water, and in 0·5 hot water. At 280° it melts, and when heated more strongly it forms a basic salt and suddenly solidifies.

Lead acetate is largely used in dyeing and calico-printing ; for the preparation of alum mordants, &c.; in the manufacture of chrome yellow and other pigments, and in medicine.

Lead forms two well-defined basic acetates —the dibasic acetate $Pb(C_2H_3O_2)_2.PbO,2H_2O$ (Wittstein, Annalen, 52, 253), formed by dissolving litharge in the normal acetate in calculated proportions ; and the tribasic acetate $Pb(C_2H_3O_2)_2.2PbO·aq$, prepared by boiling the normal acetate with excess of litharge for some time. Solutions of subacetate of lead are used in medicine as *Goulard water* and *Liquor plumbi subacetatis*.

Magnesium acetate. A basic acetate of magnesia, prepared by warming the normal acetate with magnesia, is stated to be a powerful antiseptic, disinfectant, and deodoriser (W. Kubel, Ber. 15, 684–686). A syrupy solution of the salt containing suspended magnesium hydroxide is found in commerce under the name of ' Sinodor.'

Potassium acetate $C_2H_3O_2K$ occurs in the sap of many plants, and of trees.

Its mode of preparation is similar to that of sodium acetate. It is a deliquescent crystalline solid, soluble in 0·53 part ice-cold water, and in hot water forms a solution which, boiling at 169°, contains 88 p.c. of the salt.

When chlorine gas is passed through a solution of potassium acetate, carbonic acid is evolved and a powerful, unstable, bleaching fluid is produced.

Potassium acetate may contain the same impurities as the sodium salt. The di- and tri-acetates are prepared like those of sodium.

Sodium acetate $C_2H_3O_2Na$ is formed (1) by the action of dilute acetic acid on sodium carbonate, the solution being evaporated and crystallised ; (2) by neutralisation of pyroligneous acid with soda, and evaporation and fusion of the salt to remove tarry matters ; (3) by the addition of Glauber's salt to solution of acetate of lime or of lead. The solution is decanted and filtered from the precipitated calcium or lead sulphate, evaporated and crystallised, and the crystals dissolved and recrystallised. Methods (2) and (3) are used on the manufacturing scale.

Sodium acetate forms monoclinic crystals, containing 3 molecules of water ; has a strong saline taste ; is soluble in 2·8 parts cold water and in 0·5 boiling water. The crystals melt completely at 75° and lose their water of crystallisation at 100°. By solution of this salt in ordinary strong acetic acid and rapid evaporation the di-acetate of soda is formed ; when glacial acid is used the triacetate is produced.

Sodium acetate is used for the preparation of acetic acid and in medicine ; for the preservation of meat and other foods instead of salt. The saturated solution is occasionally used for filling carriage foot-warmers.

The commercial acetate is liable to contain sulphates, chlorides and carbonates, and metallic salts. Tarry matters are frequently present from the pyroligneous acid used in its manufacture. Acetate of lime, and sulphate and carbonate of potash are occasionally added as adulterants.

For the estimation of acetic acid in commercial acetates the method of Stillwell and Gladding in a modified form is used (*v. supra*).

ALKYL ACETATES. *Acetic ethers.*

Acetic acid forms numerous acetates with organic radicles. Some of these occur in the oils from various seeds.

Amyl acetates $C_5H_{11}(C_2H_3O_2)$.

The following isomeric amyl acetates are known :—

1. Normal amyl acetate, boiling at 147·6° (Gartenmeister); at 148·4° (737 mm.) (Lieben and Rossi).

2. *Iso*amyl acetate.

3. Methyl propyl carbinyl acetate, boiling at 133°–135° (Wurtz); at 134°–137° (Schorlemmer).

4. Methyl *iso*propyl carbinyl acetate, boiling at 125° (Wurtz).

5. Diethyl carbinyl acetate, boiling at 132° (741 mm.) (Wagner and Saytzeff).

6. Tertiary amyl acetate, boiling at 124° (750 mm.) (Flavitzky).

Of these, only the second is of technical interest.

*iso*Amyl acetate, generally known as *amyl acetate* $(CH_3)_2CH \cdot CH_2CH_2O \cdot C_2H_3O$, is a colourless liquid of an odour resembling that of jargonelle pears. Sp.gr. 0·8762 15°/4° (Mendeléeff), 0·8562 22°/4° (Brühl), b.p. 138·5°–139° at 758·6 (Schiff).

It may be prepared by distilling a mixture of 1 part amyl alcohol, 1 part strong sulphuric acid, and 2 parts dried potassium acetate ; or by warming a mixture of 1 part amyl alcohol, 1 part acetic acid and 0·5 part strong sulphuric acid on the water-bath and pouring the solution when cold into excess of water. The upper layer of purified amyl acetate is separated, shaken with a strong solution of sodium carbonate, again separated, dried over calcium chloride, and re-distilled.

It may be prepared commercially from fusel oil, hydrochloric acid, and calcium acetate (Wilson, Eng. Pat. 4669). The commercial amyl acetate contains some of the other isomerides.

It is insoluble in water, but dissolves in all proportions in ether, amyl alcohol, and ordinary alcohol. The latter solution is largely used under the name of *Jargonelle pear essence* for flavouring confectionery.

Camphor, tannin, resins, &c., dissolve readily in amyl acetate. A solution of gun-cotton therein is used as a varnish, for lacquering metals, &c., and in the form of a stiff jelly, mixed with opaque substances such as china clay, as a substitute for celluloid.

It is also used in the manufacture of photographic films and in some smokeless powders.

It has been recommended for use for the production of a standard flame in photometry (J. Soc. Chem. Ind. 1885, 262).

The Hefner standard lamp burns amyl acetate as an illuminant.

Ethyl acetate. *Acetic ether* $C_2H_5(C_2H_3O_2)$ is a fragrant limpid liquid of sp.gr. 0·9072 15°/15°, b.p. 77·5° (Perkin); sp.gr. 0·92446 0°/4, b.p. 77·17° at 760 mm. (Young and Forty).

For the preparation of acetic ether 3·6 pts. by weight of commercial absolute alcohol is mixed with 9 pts. sulphuric acid with constant stirring. After standing twenty-four hours the mixture is poured on 6 pts. of fused sodium acetate (in small lumps), allowed to stand for twelve hours and distilled. The product is rectified over calcium chloride and carbonate of potash and re-distilled. Clark recommends the following process : 283 c.c. (10 oz.) of rectified alcohol (sp. gr. 0·838) are placed in a flask, and 283 c.c. of sulphuric acid (B.P.) are added with constant stirring. The liquid should be cooled externally as far as possible, allowed to stand till the temperature has sunk to 15°, and 351 grams (12¾ oz.) of dried sodium acetate added gradually with constant stirring and cooling. The liquid is distilled until 400 c.c. (14 oz.) has passed over ; this is digested for three days with 2 oz. freshly dried potassium carbonate and filtered. The filtrate is distilled on the water-bath until all but 1 oz. has passed over. On the large scale dried sodium acetate may be substituted for the potassium carbonate with advantage (*v.* further W. I. Clark, Pharm. J. [3] 1883, 777).

Ethyl acetate is soluble in 8 parts of water at 0°, and somewhat *less* soluble in water at 15°. On the other hand, 1 part water dissolves

26 parts of the acetate at 0° and 24 parts at 15°.

Commercial acetic ether usually contains less than 75 p.c. of ethyl acetate, the rest being acetic acid, alcohol, water, ether, &c. It occurs, together with other organic acetates, in vinegar and wines.

Methyl acetate $CH_3(C_2H_3O_2)$ is a colourless fragrant liquid of sp.gr. 0·9398 15°/15°, boiling at 57·5° (760 mm.) (Perkin). It occurs in wood-spirit, and in crude wood-vinegar.

Methyl acetate is best prepared by distilling a mixture of 1 part methyl alcohol, 1 part potassium acetate, and 2 parts sulphuric acid. The product is dried over calcium chloride and quicklime and redistilled. It is soluble in water, alcohol, and ether.

ACETINS. The acetins are the acetyl derivatives of glycerol, or glycerol acetates. Five of these are theoretically possible, two mono-, two di-, and one tri- derivative, according to the number and position of the hydroxyl groups attacked by the acetic acid. Only three of these compounds have been prepared so far, one in each class, and the positions which the acetyl groups take up in the mono- and di- derivatives does not appear to be experimentally proved, though they are probably terminal. Commercial acetin is a mixture of all three compounds with other products.

The following method for the preparation of mono-, di-, and tri-acetin has been described by A. C. Geitel (J. pr. Chem. 1897, [ii.] 55, 417):—

200 grams of dry glycerol are heated with 500 grams of glacial acetic acid for 8 hours, and the acetic acid and water distilled off under reduced pressure. A further quantity of 150 grams acid is then added, and the heating continued for 16 hours. *Triacetin* is isolated from the product by diluting with water and extracting with ether, and is a colourless liquid, dissolving in water to the extent of about 7 p.c. at 15°. It has a sp.gr. 1·1605 at 15° and distils without decomposition at 172°–172·50/40 mm. *Diacetin* is obtained from the remaining solution by fractionating (after concentration) under a pressure of 40 mm., when it comes over between 175°–176°. It is a soluble colourless liquid with sp.gr. 1·1769 at 15°. In order to isolate the monoacetin formed in the reaction the aqueous solution after removal of the triacetin is extracted for 8 hours with ether at 34°–35° in an extracting apparatus for liquids; the later extracts are collected separately, diluted with an equal volume of water, and, after being extracted with hot benzene, are concentrated. The monacetin thus formed is a thick syrup of sp.gr. 1·2212 at 15°. By prolonging the ether extraction still further *monacetyldiglycerol* $C_3H_5(OH)_3 \cdot O \cdot C_3H_5(OAc) \cdot OH$ may be obtained; it is a colourless liquid of sp.gr. 1·2323 at 15°. *Diacetyldiglycide* may also be separated from the monacetin by fractionation, and *triacetyldiglycerol* is also formed.

Commercial Acetin ('*Acetine*') is prepared by heating in an oil-bath a mixture of 60 parts of glycerol and 82 parts of glacial acetic acid for 12–15 hours at 120°, and gradually raising the temperature to 160° to expel the excess of acetic acid. The product is a thick liquid smelling of acetic acid and varying in colour from light yellow to dark brown, according to the purity of the glycerol used.

The value of the product depends upon the extent to which combination has taken place and this is determined by observing the specific gravity and estimating the free and combined acetic acid. The density varies between 1·1608 and 1·1896, being lowest when the free acetic acid is present in largest amount. The free and combined acetic acid are determined as follows: 50 grams of '·acetin' are diluted with water to 500 c.c. The free acid in 50 c.c. of this solution is determined by titration with normal caustic soda, using phenolphthalein as indicator. 15 c.c. of normal caustic soda are added to 10 c.c. of the acetin solution, and the combined acetic acid liberated by hydrolysis by boiling for five minutes. The excess of caustic soda remaining is a measure of the total acid present; and the amount of combined acid is found by subtracting from the amount of caustic soda used up in the hydrolysis the quantity accounted for by the free acid. The following table (Kopp and Grandmougin, Bull. Soc. Ind. Mulhouse, 1894, 112) shows the results of typical analyses:—

No.	Density	Acid free	Acid combined	Remarks
		p.c.	p.c.	
1	1·1774	9·2	46·0	A medium quality sample
2	1·1896	6·98	55·7	A good sample.
3	1·1608	23·0	43·5	Poor sample.

Acetin is used as a solvent for basic colouring matters, such as Induline and Perkin's violet. They are dissolved by being heated together for about two hours, cooling, and filtering through a silk filter. Acetin is to be preferred to ethyl and methyl tartaric acids as a solvent, as acetic acid is less injurious to the fibres than tartaric acid.

Halogen derivatives of the Acetins.

αγ-dibromo-β-acetylglycerol $(CH_2Br)_2CH \cdot OAc$ is obtained by the prolonged action of hydrogen bromide on triacetin, or by heating the mixture to 100° in sealed tubes; it boils at 130°–135° (40 mm.) and has sp.gr. 1·5880 at 15°. It has an agreeable aromatic odour, is slightly soluble in water, and readily soluble in alcohol and ether. It yields *iso*propyl alcohol on reduction.

α-bromo-βγ-diacetylglycerol $CH_2Br \cdot CH(OAc) \cdot CH_2 \cdot OAc$ is produced by the prolonged action of hydrogen bromide dissolved in acetic acid on triacetin at 0° in the dark. It boils at 150°·155° (40 mm.), and has sp.gr. 1·2905 at 15°. It yields *iso*propylene glycol on reduction.

αγ-dichloro-β-acetylglycerol $(CH_2Cl)_2CH \cdot OAc$ prepared similarly to the bromine compound, boils at 115°–120° (40 mm.), and has sp.gr. 1·1618 at 15°.

α-chloro-βγ-diacetylglycerol $CH_2Cl \cdot CH(OAc) \cdot CH_2(OAc)$ boils at 145°–150° (40 mm.), and has sp.gr. 1·1307 at 15°.

αβ-dichloromonoacetin $CH_2Cl \cdot CHCl \cdot CH_2 \cdot OAc$ is prepared by the action of acetic anhydride on chlorinated allyl alcohol, and has sp.gr. 1·1677 at 15°, but in all other respects is identical with the αγ-dichloro- compound.

α-iododiacetin $CH_2I \cdot CH(OAc) \cdot CH_2 \cdot OAc$ is

obtained by the action of sodium iodide on the corresponding chloro- compound. It is an unstable oil having a sp.gr. 1.4584 at 15°.

<div align="right">J. A. P.</div>

ACETOACETIC ACID $CH_3 \cdot CO \cdot CH_2 \cdot CO_2H$ is a thick acid liquid miscible with water in all proportions. It is prepared from its ethyl ester by leaving $4\frac{1}{2}$ parts of ester in contact with 2·1 parts of potash and 80 parts of water for 24 hours and acidifying with sulphuric acid. It is extracted from the solution with ether.

It is very unstable and readily decomposes below 100° into acetone and carbon dioxide. It yields a violet colouration with ferric chloride and forms ill-characterised amorphous salts, $BaA_2,2H_2O$ and $CuA_2,2H_2O$, when treated with the corresponding carbonate.

Acetoacetic acid appears in the urine of diabetic patients, and indicates defective oxidation. Its detection and estimation have been the subject of much controversy and investigation. Arnold (Chem. Zentr. 1899, ii. 146) makes use of a colour reaction with acetophenone, which will show 1 part in 10,000, but is affected to some extent by the presence of acetone. Riegler (Chem. Soc. Abstr. 1903, ii. 112) employs the colour produced by the addition of sulphuric and iodic acids, which he states to be unaffected by the presence of sugars, leucine, tyrosine, or acetone. Bondi (Chem. Zentr. 1906, i. 707) recommends the use of a solution of iodine and the detection of acetoacetic acid by the characteristic smell of the iodacetone produced; but Lindemann (*ibid.* 717) says that this smell is not characteristic of acetoacetic acid. Mayer adds the urine to a very dilute solution of ferric chloride in brine, when, in the presence of acetoacetic acid, a claret-red ring is formed. When the red colour is only just visible, the liquid may be assumed to contain 0·01 p.c. of the acid. A blank test performed after boiling the acid for five minutes should give no colour (Chem. Zentr. 1906, i. 406).

Messinger's process as modified by Huppert (Analyse des Harns, 1898) estimates the total amount of acetone and acetoacetic acid present with fair accuracy, and the acetone may be estimated separately with considerable exactitude by the method of Folin (J. Biol. Chem. 1907, 3, 177), in which it is aspirated out of the liquid into iodine and potash, and the resulting iodoform weighed.

Methyl acetoacetate $CH_3 \cdot CO \cdot CH_2 \cdot CO_2Me$ is prepared by heating together methyl acetate and sodium under a reflux condenser and subsequently distilling in a stream of carbon dioxide. It is a colourless liquid, easily miscible with water, which boils at 169°–170° and has a sp.gr. 1·0917 at 4°; 1·0809 at 15°; and 1·0724 at 25°. It is decomposed on boiling with water into carbon dioxide, acetone, and methyl alcohol. With ferric chloride it yields a deep red colouration.

Ethyl acetoacetate (acetoacetic ether) $CH_3 \cdot CO \cdot CH_2 \cdot CO_2Et$ and $CH_3 \cdot C(OH):CH \cdot CO_2Et$, was discovered by Geuther in 1863, and independently by Frankland and Duppa in 1865. It is a colourless, slightly syrupy liquid, with a pleasant odour. It boils at 180·6°–181·2°/754 mm. (Brühl); 180°–180·3° /754·5 mm. (Schiff); 71°/12·5 mm. and 100·2°/80mm. (Kahlbaum). It has a specific gravity 1·0465 0°/4° (Schiff); 1·0282 20°/4° (Schaum).

Ethyl acetoacetate is prepared by the action of sodium on ethyl acetate. The following details of the method are given by Conrad (Annalen, 186, 214): 100 grams of sodium are added to 1000 grams of pure ethyl acetate, and after the reaction has moderated considerably, the whole is heated on a water-bath under a reflux condenser for 2–2½ hours until all the sodium has disappeared. To the warm mass 550 grams of 50 p.c. acetic acid are added, and after cooling 500 c.c. of water. The whole is well shaken, and the upper layer separated, washed with a little water, and fractionated. The fractions 100°–130°, 130°–165°, 165°–175°, 175°–185°, 185°–200° are collected separately and refractionated twice. The yield is 175 grams of product boiling at 175°–185°, and from the fraction boiling below 100°, 350–400 grams of ethyl acetate may be recovered after removing the alcohol by salting out.
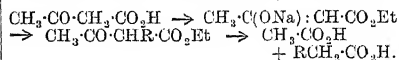
Ethyl acetoacetate is neutral to litmus, but forms salts with sodium, copper, and other metals by replacement of hydrogen. Only one atom of hydrogen can be replaced by sodium, but if the sodium in the resulting compound is replaced by an alkyl radicle a second hydrogen atom may then be replaced. Ferric chloride produces a violet colouration. With sodium bisulphite a crystalline addition product $C_6H_{10}O_3$, $NaHSO_3$ is formed. On heating for a long time, or leading the vapour through a hot tube, acetone, alcohol, dehydracetic acid, and methane are formed. Sodium amalgam reduces it to *β-hydroxy butyric* acid $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$. It condenses with hydroxylamine, but does not form an oxime, as internal condensation takes place, resulting in the production of *methyl isoxazolone* $CH_3 \cdot C \cdot CH_2 \cdot CO$ which is converted by

$$N-----O$$

alkalis into salts of β-oximinobutyric acid.

Applications in Synthesis.—By means of ethyl acetoacetate fatty acids, ketones, and many ring compounds may be prepared.

Fatty acids may be obtained by dissolving sodium (1 atom) in absolute alcohol, adding ethyl acetoacetate (1 mol.) followed by an alkyl halogen compound (1 mol.). The resulting alkyl derivative is treated with strong alkalis, when the molecule is hydrolysed with formation of acetic acid and the desired alkyl acetic acid.
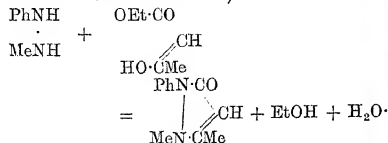
$CH_3 \cdot CO \cdot CH_2 \cdot CO_2H \rightarrow CH_3 \cdot C(ONa):CH \cdot CO_2Et$
$\rightarrow CH_3 \cdot CO \cdot CHR \cdot CO_2Et \rightarrow CH_3 \cdot CO_2H + RCH_2 \cdot CO_2H.$

If the hydrolysis is brought about by *dilute acids* instead of concentrated alkalis, the molecule is differently divided, producing ketones.

$CH_3 \cdot CO \cdot CHR \cdot CO_2Et \rightarrow CH_3CO \cdot CH_2R + EtOH + CO_2.$
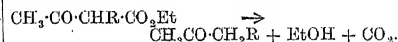
Dialkyl acetic acids and ketones may be produced by introducing a second alkyl radicle into the molecule by a similar process after the first has entered, but the two cannot be introduced together in one operation.

Pyrazolones, of which the most important industrially is *antipyrine,* are produced by the condensation of ethyl acetoacetate with hydrazines. Antipyrin (1-*phenyl* 2:3-*dimethyl-5-pyrazolone*) is prepared from symmetrical methyl
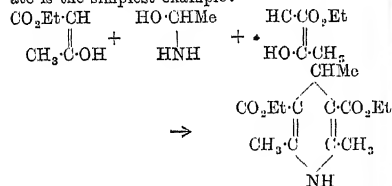
<div align="right">c 2</div>

phenylhydrazine and ethyl acetoacetate (*v.* also PYRAZOLE and ANTIPYRINE).

$$\text{PhNH} \atop \text{MeNH} \Big\} + \quad \begin{matrix} \text{OEt·CO} \\ \cdot \\ \diagup\text{CH} \\ \text{HO·CMe} \end{matrix}$$

$$= \quad \begin{matrix} \text{PhN·CO} \\ | \\ \diagup\text{CH} + \text{EtOH} + \text{H}_2\text{O·} \\ \text{MeN·CMe} \end{matrix}$$

Quinolines may be prepared by first making the anilide of ethyl acetoacetate by heating with aniline at 110°, and afterwards heating this product with concentrated hydrochloric acid. $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot NHPh$ changes into $CH_3 \cdot C(OH) : CH \cdot C(OH) : NPh$, and readily condenses to 1-*hydroxy-4-methylquinoline*

HO·CMe
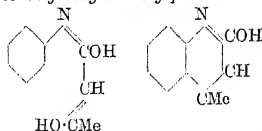
Pyridines (*v.* also BONE OIL) are obtained by condensing ethyl acetoacetate with aldehyde ammonias. Ethyl dihydrocollidine dicarboxylate is the simplest example:

$$\begin{matrix} \text{CO}_2\text{Et·CH} \\ \| \\ \text{CH}_3 \cdot \text{C·OH} \end{matrix} + \begin{matrix} \text{HO·CHMe} \\ | \\ \text{HNH} \end{matrix} + \begin{matrix} \text{HC·CO}_2\text{Et} \\ \cdot \| \\ \text{HO·C·CH}_2 \\ \text{CHMe} \end{matrix}$$

$$\rightarrow \quad \begin{matrix} \text{CO}_2\text{Et·C} \quad \text{C·CO}_2\text{Et} \\ \| \quad\quad \| \\ \text{CH}_3 \cdot \text{C} \quad\quad \text{C·CH}_3 \\ \diagdown \quad \diagup \\ \text{NH} \end{matrix}$$

Pyrones.—Dehydracetic acid, *a*-methyl *β*-acetylpyrone, is produced on heating ethyl acetoacetate for a considerable time.

Constitution.—The constitution of ethyl acetoacetate and its sodium derivatives was for many years a subject of discussion by Frankland and Duppa, Geuther, Claisen, Laar, Wislicenus, Brühl, Perkin, and others. The general opinion is that ethyl acetoacetate consists of a mixture of the two forms, ketonic $CH_3 \cdot CO \cdot CH_2 \cdot CO_2Et$, and enolic $CH_3 \cdot C(OH) : CH \cdot CO_2Et$. The freshly prepared substance is practically a pure ketone, but on keeping it changes partially into the enolic form, and when equilibrium is reached about 10 p.c. of the enolic form is present at ordinary temperatures. The sodium compound is a derivative of the enolic form.

Alkyl derivatives of ethyl acetoacetate.

1. *Mono-substituted alkyl derivatives.*

Ethyl methylacetoacetate $CH_3 \cdot CO \cdot CHMe \cdot CO_2Et$ boils at 186·8°, and has sp.gr. 1·009 at 6°. Prepared from methyl iodide and sodium acetoacetate (Geuther, J. 1865, 303).

Ethyl ethylacetoacetate $CH_3 \cdot CO \cdot CHEt \cdot CO_2Et$ boils at 195°–196°, and has sp.gr. 0·9834 at 16°. It is readily decomposed by baryta or alcoholic potash into alcohol, carbon dioxide and methyl propyl ketone; and by dry sodium ethoxide into acetic and butyric esters (Miller, Annalen, 200, 281 ; Wedel, Annalen, 210, 100 ; Frankland and Duppa, Annalen, 138, 215; Wislicenus, Annalen, 186, 187).

Ethyl propylacetoacetate $CH_3 \cdot CO \cdot CHPr^a \cdot CO_2Et$ boils at 208°–209°, and has sp.gr. 0·981 at 0°/4°. It is prepared by adding to a solution of 27 grams of sodium in 270 grams absolute alcohol, 152·7 grams ethyl acetoacetate, followed gradually by 206 grams propyl iodide.

Ethyl isopropylacetoacetate $CH_3 \cdot CO \cdot CHPrβ \cdot CO_2Et$ boils at 201°/758·4, and has sp.gr. 0·9805 at 0°.

Ethyl isobutylacetoacetate $CH_3 \cdot CO \cdot CH(CH_2 \cdot CHMe_2) \cdot CO_2Et$ boils at 217°–218°, and has sp.gr. 0·951 at 17·5° (Rohn, Annalen, 190, 306 ; Minter, Ber. 1874, 501).

Ethyl isoamylacetoacetate $CH_3 \cdot CO \cdot CH(CH_2 \cdot CH \cdot CHMe_2)CO_2Et$ boils at 227°–228° (Peters, Ber. 1887, 3322).

Ethyl amylacetoacetate $CH_3 \cdot CO \cdot CH(C_5H_{11}) \cdot CO_2Et$ boils at 242°–244° (Ponzio and Prandi, Gazz. chem. ital. 28, ii. 280).

Ethyl heptylacetoacetate boils at 271°–273°, and has sp.gr. 0·9324 at 17·7°.

Ethyl octylacetoacetate boils at 280°–282°, and has sp.gr. 0·9354 at 18°·5/17·5°.

2. *Di-substituted alkyl derivatives.*

Ethyl dimethylacetoacetate $CH_3 \cdot CO \cdot CMe_2 \cdot CO_2Et$ boils at 184°, and has sp.gr. 0·9913 at 16°.

Ethyl methylethylacetoacetate $CH_3 \cdot CO \cdot CMeEt \cdot CO_2Et$ boils at 198 , and has sp.gr. 0·947 at 22°/17°·5.

Ethyl methylpropylacetoacetate $CH_3 \cdot CO \cdot CMe Pr \cdot CO_2Et$ boils at 214°, and has sp.gr. 0·9575 at 17°/4°.

Ethyl diethylacetoacetate $CH_3 \cdot CO \cdot CEt_2 \cdot CO_2Et$ boils at 218°, and has sp.gr. 0·9738 at 20°.

Ethyl dipropylacetoacetate $CH_3 \cdot CO \cdot CPr_2 \cdot CO_2Et$ boils at 236°, and has sp.gr. 0·9585 at 0°/4°.

Ethyl diisobutylacetoacetate boils at 250°–253°, and has sp.gr. 0·947 at 10°.

Ethyl diheptylacetoacetate boils at 332°, and has sp.gr. 0·891 at 17·5°/17·5°.

Ethyl dioctylacetoacetate boils at 261° 90 mm , 340°–342° /760 mm.

ACETOL. Obtained as an ester of salicylic acid by condensing sodium salicylate with monochloracetone $OH \cdot C_6H_4 \cdot COO \cdot CH_2 \cdot CO \cdot CH_3$. Forms needles from solution in alcohol, m.p. 71° ; sparingly soluble in warm water (Fritsch, E. P. 3961, 1893 ; J. Soc. Chem. Ind. 1891, 274).

ACETOMETER. A hydrometer graduated to indicate the strength of commercial acetic acid according to its density.

ACETONE C_3H_6O or $CH_3 \cdot CO \cdot CH_3$. *Dimethyl ketone.* A product of the destructive distillation of acetates ; obtained by Liebig from lead acetate (Annalen, 1, 225) and further examined by Dumas (Ann. Chim. Phys. [2] 49, 208), who first determined its composition. Acetone is also produced in the dry distillation of wood (Völckel, Annalen, 80, 310 ; J. Soc. Chem. Ind. 16, 667, 722 ; 27, 798); of citric acid (Robiquet, B. J. 18, 502); of sugar, starch, and gums with lime (Frémy, Annalen, 15, 279 ; J. Soc. Chem. Ind. 21, 541, 1096). By oxidation of proteïd substances with iron salts (Blumenthal and Neuberg, Chem. Zentr. 1901, i. 188 ; Ingler, Beitr. Chem. Phys. Path. 1902, i. 583), and by heating citric acid with potassium permanganate (Péan de St. Gilles, J. 1858, 585; Sabbatani, Atti Acad. Sci. Torino, 1900, 35, 678); and by the oxidation of *iso*valeric acid (Crossley and Le Sueur, Chem. Soc. Trans. 1899, 165).

Preparation.—1. Acetone can be obtained by distilling a mixture of 1 part of caustic lime and 2 parts of crystallised lead acetate (Zeise, Annalen, 33, 32); but is usually prepared by the dry distillation of barium acetate at a moderate heat. Calcium acetate can also be employed, but the temperature required is greater, and the product is contaminated with impurities, such as *dumasin*, an isomeride of mesityl oxide; but according to Becker (J. Soc. Chem. Ind. 26, 279) a lower temperature is required if the calcium salts are made quite neutral and the formation of free lime is prevented by the introduction of a stream of dry carbon dioxide. Magnesium or strontium acetates can also be used. Industrially, acetone can be prepared by passing the vapour of acetic acid into air-tight vessels heated to 500°, containing some porous substances saturated with lime or baryta (J. Soc. Chem. Ind. 18, 128, 824; Bauschlicker, D. R. P. 81914); also by passing a continuous current of pyroligneous acid over a heated acetate capable of forming acetone (J. Soc. Chem. Ind. 25, 634; 26, 1002; 27, 277). An improved method is also described by Wenghöffer (D. R. P. 144328; compare also J. Soc. Chem. Ind. 14, 987; 20, 1130; 22, 297).

According to Squibb (J. Soc. Chem. Ind. 1896, 231; J. Amer. Chem. Soc.), pure acetone for use in the preparation of smokeless powders can be obtained by subjecting acetates mixed with an excess of calcium hydroxide to destructive distillation and to the action of superheated steam.

2. From wood-spirit acetone can be separated by distilling over calcium chloride. The product obtained by these methods can readily be purified by converting the acetone into its crystalline compound with acid sodium (or potassium) sulphite, crystallising this, and subsequently distilling with aqueous sodium carbonate; the distillate is then treated with concentrated calcium chloride solution and the ethereal layer rectified over solid chloride. According to Conroy (J. Soc. Chem. Ind. 19, 206), it should be purified by distillation over sulphuric acid (Dott, J. Soc. Chem. Ind. 27, 272), whilst Arnoult (*ibid.* 27, 679) recommends treatment with oxidising agents.

Acetone has been prepared synthetically from zinc methyl and acetyl chloride (Freund, Annalen, 118, 11). It occurs in the urine, blood, and brain of calcium diabetic patients.

Properties.—Acetone is a limpid, mobile liquid, having an agreeable odour and a peppermint-like taste. It is very inflammable and burns with a white smokeless flame, b.p. 56·3° (Regnault); sp.gr. 0·8144 at 0°, 0·79945 at 13·9° (Kopp, Annalen, 64, 214); b.p. 56·53° (corr.) and sp.gr. 0·81858 at 0°/4° (Thorpe. Chem. Soc. Trans. 37, 212); sp.gr. 0·81378 at 0°/4°, 0·79705 at 15°/4°, 0·77986 at 30°/°4 (Saposchnikoff, J. Russ. Phys. Chem. Soc. 28, 229); m.p.−94·9° (Ladenburg and Krügel, Ber. 32, 1821; Formenti, L'Orosi, 1900, 23, 223). Acetone is miscible in all proportions with water, alcohol, ether, and many ethereal salts; it can be separated from °its aqueous solution by the addition of calcium chloride, and dissolves many fats and resins. It is also an excellent solvent for acetylene and tannins (Trimble and Peacock, Pharm.

J. 53, 317). Acetone is used in perfumery and in pharmacy; in the manufacture of smokeless powders; of cordite and of celluloid articles (Marshal, J. Soc. Chem. Ind. 23, 24, 645), also in the preparation of iodoform (Teeple, J. Amer. Chem. Soc. 26, 170; Abbott, J. Phys. Chem. 7, 83); of chloroform (Squibb, J. Amer. Chem. Soc. 1896, 231; Orndorff and Jessel, Amer. Chem. J. 10, 363; Dott, *l.c.* 271); and in the presence of sodium sulphite it can be used as a good substitute for alkali in photographic developers (Lumière and Segewetz, Bull. Soc. chim. 15, [3] 1164; Mon. Sci. 1903, 257, 568; Eichengrün, Zeitsch. angew. Chem. 1902, 1114). When its vapour is passed through a red-hot copper tube, a very small proportion of tarry products containing naphthalene is obtained together with a large volume of gas having the composition : carbon monoxide, 39·23 p.c.; methane, 37·58 p.c.; hydrogen, 17·54 p.c.; and ethylene, 5·65 p.c. (Barbier and Roux, Compt. rend. 102, 1559). Dehydrating agents readily act on acetone and convert it into condensation products; thus, caustic lime converts acetone into mesityl oxide $C_6H_{10}O$ and phorone $C_9H_{14}O$ when the action is allowed to continue for a week (Fittig, Annalen, 110, 32), and, together with smaller proportions of other products, these two compounds are also formed when it is saturated with hydrogen chloride and allowed to stand for 8 to 14 days (Baeyer, Annalen, 140, 297): with zinc chloride terpene condensation products are formed (Raikow, Ber. 30, 905). Distillation with concentrated sulphuric acid converts acetone into mesitylene, mesityl oxide, phorone, and *iso*durene and other substances (Orndorff and Young, Amer. Chem. J. 15, 249). A similar result is obtained when it is heated with boron fluoride. The action of nitric acid and nitric oxide on acetone has been studied by Newbury and Orndoff (Amer. Chem. J. 12, 517), Behrend and Schmitz (Annalen, 277, 310), Behrend and Tryller (Annalen, 283, 209), Apetz and Hell (Ber. 27, 933), Traube (Annalen, 300, 81), McIntosh (Amer. Chem. Soc. 27, 1013); of hydrogen peroxide by Baeyer and Villiger (Ber. 32, 3625; 33, 174, 858), Pastureau (Compt. rend. 140, 1591), Wolffenstein (Ber. 28, 2265); of thionyl chloride by Loth and Michaels (Ber. 27, 2540); and of hypophosphorous acid by Marie (Compt. rend. 133, 219).

Sodium in the presence of water reduces acetone to *iso*propyl alcohol and pinacone (Fittig, Annalen, 110, 25; 114, 54; Städeler, Annalen, 111, 277; Friedel, Annalen, 124, 329), but when the materials are quite dry and air is excluded, sodium acetonate is formed (Freer, Amer. Chem. J. 12, 355; 13, 308; 15, 582; Taylor, Chem. Soc. Trans. 1906, 1258; Bacon and Freer, Philippine J. Sci. 1907, 2, 67). Red-hot magnesium acts on acetone, yielding hydrogen and allylene, whilst magnesium amalgam forms magnesium acetonate which is rapidly decomposed by water, yielding pinacone hydrate (Keiser, Amer. Chem. J. 18, 328; Conturier and Meunier, Compt. rend. 140, 721). Chlorine, bromine, and iodine in the presence of alkalis convert acetone into chloroform, bromoform, and iodoform respectively.

Reactions.—When quite pure acetone should remain perfectly colourless on exposure to light, and should not be attacked by potassium

permanganate in the cold; in the presence of alkali, however, and on warming, carbonic and oxalic acids are formed (Cochenhausen, J. pr. Chem. 166, 451; Conroy, J. Soc. Chem. Ind. 19, 206; Fournier, Bull. Soc. chim. 1908, 3, 259). Acetone, when treated with aqueous potash and iodine, yields iodoform (Lieben). Gunning (Zeitsch. anal. Chem. 24, 147) has modified this reaction to render it available when alcohol is present by employing ammonia and a solution of iodine in ammonium iodide. Another test proposed by Reynolds (*ibid.* 24, 147) is based on the fact that mercuric oxide is soluble in acetone in the presence of potassium hydroxide; the suspected liquid is mixed with a solution of mercuric chloride rendered strongly alkaline with alcoholic potash, and after shaking the mixture is filtered and the filtrate tested for mercury by means of ammonium sulphide or stannous chloride. Denigès (Compt. rend. 126, 1808; 127, 963; Bull. Soc. chim. 13, [3] 543; 19, [3] 754) recommends the use of the additive compound formed by acetone with mercury sulphate, for detecting acetone in methyl and ethyl alcohol (Oppenheimer, Ber. 32, 986). Penzoldt (Zeitsch. anal. Chem. 24, 147) adds to the suspected liquid orthonitrobenzaldehyde, which in presence of caustic alkali combines with acetone to form indigo. Another delicate test is to add sodium hydroxide, hydroxylamine and pyridine, then ether and bromine until the solution is yellow, hydrogen peroxide is now added when, if acetone is present, the solution becomes blue (Stock); dimethyl *p*-phenylenediamine produces a red colouration which changes to violet on addition of alkali or acid (Malerba, Zeitsch. anal. Chem. 37, 690). Similar colour reactions are obtained by adding a few drops of sodium nitroprusside to a mixture of acetone and a primary aliphatic amine (Rimini, Chem. Zentr. 1898, 2, 132). Of all these tests Lieben's is perhaps the most sensitive. To detect acetone in urine a strong solution of sodium nitroprusside is added, then the mixture made alkaline with potash, when a red colouration is produced which changes to violet on addition of acetic acid (Legal, J. Pharm. Chim. 1888, 17, 206; Denigès, Bull. Soc. chim. [3] 15, 1058). According to Egeling (Chem. Zentr. 1894, ii. 457), it is best to use ammonia, when a brilliant violet colour is at once produced: this reaction is not given by aldehyde. For other methods of detecting and estimating acetone, compare Arachequesne, Compt. rend. 110, 642; Collischonn, Zeitsch. anal. Chem. 29, 562; Squibb, J. Amer. Chem. Soc. 18, 1068; Kebler, *ibid.* 19, 316; Schwicker, Chem. Zeit. 15, 914; Strache, Monatsh. 13, 299; Klar, J. Soc. Chem. Ind. 15, 299; Hintz, Zeitsch. anal. Chem. 27, 182; Sternberg, Chem. Zentr. 1901, i. 270; Keppeler, Zeitsch. angew. Chem. 18, 464; Vaubel and Schleuer, *ibid.* 18, 214; Jolles, Ber. 39, 1306; Auld, J. Soc. Chem. Ind. 25, 100; Heikel, Chem. Zeit. 32, 75.

(For estimating acetone in wood spirit, *see* Arachequesne, *l.c.*; Vignon, Compt. rend. 110, 534; 112, 873; and in urine, *see* Huppert, Zeitsch. anal. Chem. 29, 632; Salkowski, J. Pharm. Chim. 1891, 194; Geelmuyden, Zeitsch. anal. Chem. 35, 503; Willen, Chem. Zentr. 1897, i. 134; Martz, ii. 232; Argenson, Bull. Soc. chim. 15, [3] 1055; Studer, Chem. Zentr. 1898, i. 1152; Mallat, J. Pharm. 1897, 6296;

Sabbatani, Chem. Zentr. 1899, ii. 22; Riegler, Zeitsch. anal. Chem. 40, 94; Vournasos, Bull. Soc. chim. 31, [3] 137; Graaff, Pharm. Weekblad, 1907, 44, 555; Folin, J. Biol. Chem. 1907, 3, 177; Monimart, J. Pharm. Chem. 1892, 26, 392; Heikel, *l.c.*; Hart, J. Biol. Chem. 1908, 4, 477.)

Derivatives.—Acetone combines directly with a large number of substances yielding well-characterised additive compounds. 1. *Compounds with alkaline sulphites*:—Acetone forms definite crystalline compounds when shaken with concentrated solutions of the acid sulphites (bisulphites) of the alkali metals (Precht, Phot. Centr. 1902, 8, 301; Kerp, Kaiserl. Gesundh. 1904, 21, 40; Rothwood, Monatsh. 26, 1545). The *potassium* salt $C_3H_6O,KHSO_3$, and the *sodium* salt $C_3H_6O,NaHSO_3$, crystallise in nacreous scales (Limpricht, Annalen 93, 238); the *ammonium* salt C_3H_6O,NH_4HSO_3 crystallises in laminæ (Städeler, Annalen 111, 307). The *barium* salt has formula $2(C_3H_6O,Ba(SO_3H)_2).H_2O$ (Fargard, J. Pharm. Chim. 1895, 2, 145). These salts yield acetone when heated with aqueous potash. —2. *Compounds with chloroform* (Willgerodt, Ber. 14, 2451; 15, 2308; Cameron and Holly, Chem. Zentr. 1898, ii. 277; Jocitsch, *ibid.* 1899, i. 606; Willgerodt and Dürr, J. pr. Chem. 148, 283). —3. *Compounds with hydrogen cyanide* (Urech, Annalen, 164, 255):—Acetone yields acetonecyanhydrol C_4H_7NO, b.p. 120°, when added to anhydrous hydrogen cyanide; and diacetonecyanhydrol $C_7H_{13}NO_2$, a crystalline substance, when treated with a 25 p.c. solution (aqueous) of hydrogen cyanide (Tiemann and Friedländer, Ber. 14, 1965); with 3·3 p.c. hydrogen cyanide acetonecyanhydrin is obtained in the dark, but in the light a mixture of products is formed (Silber, Ber. 38, 1671).— 4. *Compounds with ammonia:* Ammonia unites with acetone in the cold with the elimination of the elements of water; the reaction, however, proceeds more quickly if the temperature is raised to 100°, or if dry ammonia gas is passed into boiling acetone. Several bases, diacetonamine $C_6H_{13}NO$, triacetonamine $C_9H_{17}NO$, triacetonediamine $C_9H_{18}N_2O$, and dehydrotriacetonamine $C_9H_{15}N$: the last two in very small quantity only, have been obtained by these methods, the relative proportions in which they are formed varying with the temperature and time employed. These bases and their derivatives have been examined by Heintz (Annalen, 174, 133; 175, 252; 178, 305, 326; 181, 70; 183, 276; 189, 214; 191, 122; 198, 42, 87; 201, 90; 203, 336) and by Sokolow and Latschinow (Ber. 7, 1384), Ruhemann and Carnegie (Chem. Soc. Trans. 1888, 424), Rügheimer (Ber. 21, 3325; 25, 1562), Harries (Annalen, 296, 328), Franchimont and Friedmann (Rec. Trav. Chim. 1907, 223), Gabriel and Colman (Ber. 35, 3805), Kohn and Lindauer (Monatsh. 23, 754), Kohn (Annalen, 351, 134; Monatsh. 24, 765, 773; 25, 135, 817, 850; 28, 429, 508, 529, 537, 1040); they yield well-crystallised salts, and can be separated from one another by means of their oxalates. Methylamine also gives corresponding compounds with acetone, but dimethylamine yields dimethyldiacetonamine as the sole product (Köttschmann, Annalen, 197, 27).

Thioacetones have been studied by Baumann and Fromm (Ber. 22, 1035, 2592).

Acetone forms compounds with mercuric sulphate (Denigès, *l.c.*; Oppenheimer, *l.c.*), with mercuric oxide (Auld and Hantzsch, Ber. 38, 2677; Lasserre, J. Pharm. Chim. 1890, 22, 246), with mercuric cyanide (Marsh and Struthers, Chem. Soc. Trans. 1905, 1878), with mercuric iodide (Gernez, Compt. rend. 137, 255; Marsh and Struthers, Chem. Soc. Proc. 1908, 266), and with mercuric nitrate (Hofmann, Ber. 31, 2212). Metallic derivatives of the type $CH_3 \cdot CO \cdot CH_2K$ are obtained by the electrolysis of acetone solutions of potassium or sodium iodides or of potassium thiocyanate (Levi and Voghera, Gazz. chim. ital. 35, i. 277).

Acetone yields substitution derivatives when acted upon with chlorine or bromine (Bischoff, Ber. 5, 863, 963; 8, 1329). The following derivatives have been obtained:—Monochloracetone (Henry, Ber. 5, 190; Mulder, Ber. 5, 1009; Barbaglia, Ber. 7, 467; Linnemann, Annalen, 134, 171; Koenigs and Wagstaffe, Ber. 26, 554; Wislicenus, Kircheisen and Sattler, *ibid.* 26, 908; Fritsch, *ibid.* 26, 597; Tcherniac, Ber. 25, 2629; Kling, Bull. Soc. chim. [3] 33, 322); unsymmetrical dichloracetone (Fittig, Annalen, 110, 40; Borsche and Fittig, Annalen, 133, 112; Erlenbach, Annalen, 269, 46; Tcherniac, *l.c.*; Fritsch, *l.c.*; McIntosh, Chem. Soc. Trans. 1905, 790); symmetrical dichloracetone (Barbaglia, *l.c.*; Fritsch, *l.c.*); trichloracetone (Bischoff, *l.c.*; Kraemer, Ber. 7, 252; Perrier and Prost, Compt. rend. 140, 146; Hantzsch, Ber. 21, 242); tetrachloracetone (Bischoff, Levy, Witte and Curchod, Annalen, 252, 330, 254, 83; Levy and Jedlicka, Ber. 21, 318); and pentachloracetone (Cloëz, Bull. Soc. chim. [2] 39, 638; Fritsch, Annalen, 279, 310 and *l.c.*; Levy and Jedlicka, *l.c.*). The corresponding bromoderivatives, with the exception of tribromacetone, are obtained by the direct action of bromine upon acetone (Mulder, J. 1864, 330; McIntosh, *l.c.*; Lapworth, Chem. Soc. Trans. 1904, 33), also by other methods (Hjelt and Siven, Ber. 21, 3288; Norton and Wistenhoff, Amer. Chem. J. 10, 213; Hantzsch, *l.c.*). Other halogen derivatives (J. Soc. Chem. Ind. 16, 933; Hantzsch, *l.c.* and Ber. 22, 1238) and the compounds of acetone with the halogen acids (Archibald and McIntosh, Chem. Soc. Trans. 1904, 924) have been described.

Acetone forms a large number of condensation products and derivatives with other organic compounds: Cyanacetones (Hantzsch, Ber. 23, 1472; Tcherniac, Ber. 25, 2607, 2621; Kowppa, Ber. 33, 3530). Acetone dioxalic ester obtained by the action of sodium cthylate on a mixture of acetone and oxalic ester is converted when treated with sodium ethoxide to a dienolic substance forming lemon-yellow needles, m.p. 98°, and dyeing wool in alcoholic solution. It is the first nitrogen free dye-stuff of the fatty series yet obtained (Willstätter and Pummerer, Ber. 37, 3733). Pseudocyclocitralidene acetone and its homologues have an odour of violets, and are suitable for use in perfumes (J. Soc. Chem. Ind. 24, 290).

For acetone dicarboxylic acid and its derivatives, *see* Ormerod, Chem. Soc. Proc. 1906, 205; Denigès, Compt. rend. 128, 680; Lippmann, Ber. 41, 3981; for acetonyl acetone and its derivatives, *see* Knorr, Ber. 22, 168, 2100; Claisen and Ehrhardt, Ber. 22, 1009; Zincke

and Kegel, Ber. 23, 230; Claisen, Ber. 25, 3164; the azo- (Bulow and Schlotterbeck, Ber. 35, 2187) and diazo- derivatives of acetonyl acetone, have dyeing properties (Faurel, Compt. rend. 128, 318).

Acetone, with diazobenzene chloride in the presence of alkali, yields a compound $C_{15}H_{14}ON_2$, m.p. 134°–135°, which has dyeing properties (Bamberger and Wulz, Ber. 24, 2793). For other condensation products compare Boessneck, Ber. 21, 1906; Pechmann and Wehsarg, *ibid.* 2989, 2994; Franke and Kohn, Monatsh. 19, 354; 20, 876; Spier, Ber. 28, 2531; Perkin and Thorpe, Chem. Soc. Trans. 1896, 1482; Weidel, Monatsh. 17, 401; Micko, *ibid.* 442; Stobbe, Ber. 28, 1122; Cornelson and Kostanecki, Ber. 29, 240; Claisen, *ibid.* 2931; Röhmer, Ber. 31, 281; Pfitzinger, J. pr. Chem. 164, 283; Freer, Amer. Chem. J. 17, 1; Barbier and Bouveault, Compt. rend. 118, 198; Haller and March, Compt. rend. 139, 99; Straus, Ber. 37, 3293; Harries and Ferrari, Ber. 36, 656; Ulpiani and Bernardini, Atti R. Accad. Lincei, 1904, 13, 331; Pechmann and Sidgwick, Ber. 37, 3816; Duntwitz, Monatsh. 27, 773; Knoevenagel, Ber. 39, 3451, 3457; Purdie, Chem. Soc. Trans. 1906, 1200; Richard, Compt. rend. 145, 129. Diacetones and their derivatives have been studied by Combes (Compt. rend. 108, 1252; Behal and Auger, Compt. rend. 109, 970; Claisen and Stylos, Ber. 21, 141); derivatives of triacetone by Weinschenk (Ber. 34, 2185).

ACETONECHLOROFORM, *aaa-trichlor-β-hydroxy-β-methylpropane (Chloretone)* $(CH_3)_2 \cdot C(OH) \cdot CCl_3$, prepared by slowly adding powdered potassium hydroxide (3 parts) to a cooled mixture of acetone (5 parts) and chloroform (1 part) (Willgerodt, J. pr. Chem. [2] 37, 361) is a white crystalline compound, b.p. 167°, melting near but above 97°; it has a camphor-like odour, is soluble in hot, sparingly soluble in cold water, and crystallises well from ether, alcohol, acetic acid, acetone, or chloroform; it forms no definite hydrate, but the system acetone-chloroform/water presents a quadruple point for the solid, two solutions and the vapour at 75·2° (Cameron and Holly, J. Phys. Chem. 1898, 2, 322). The *acetate* $(CH_3)_2 \cdot C(OAc) \cdot CCl_3$ boils at 191°. The *benzoate* $(CH_3)_2 \cdot C(OBz) \cdot CCl_3$ boils at 282° (Willgerodt and Dürr, J. pr. Chem. [2] 39, 283). Acetonechloroform is reduced by zinc-dust and alcohol, forming dichloro*iso*butylene, *iso*crotylchloride, and *iso*butylene (Jocitsch, J. Russ. Phys. Chem. Soc. 1898, 30, 920); and is decomposed by water at 180°, yielding hydrogen chloride and hydroxy*iso*butyric acid (Willgerodt, Ber. 1882, 15, 2305). By the action of benzene in presence of aluminium chloride the chlorine atoms of acetonechloroform are replaced wholly or in part by phenyl residues, and the compounds *diphenylchloromethyl dimethyl carbinol* $CPh_2Cl \cdot CMe_2 \cdot OH$ b.p. 239°; *phenyldichloromethyl dimethyl carbinol* $CPhCl_2 \cdot CMe_2 \cdot OH$ b.p. 217°; and *triphenylmethyl dimethyl carbinol* $CPh_3 \cdot CMe_2 \cdot OH$ b.p. 260°, have been prepared, and similar compounds are obtained using toluene or *p*-xylene (Willgerodt, J. pr. Chem. [2] 37, 361).

Acetonechloroform is a powerful germicide, a satisfactory surgical dressing, and hypnotic for internal use (Aldrich and Houghton, Amer. J. Physiol. 1900, 3, 26); it is used as a specific for sea-sickness (Merck, Ann. Report,

1907, 1), and a 1–2 p.c. solution is used under the name of *anesin* for producing local anæsthesia (Cohn, Pharm. Zentr. H. 40, 33).

ACETONEDICARBOXYLIC ACID *v.* KETONES.

ACETONE OIL is the oily residue remaining after the separation of acetone from the products of the dry distillation of calcium acetate. It can also be prepared by the dry distillation of the lime salts obtained by neutralising fleece washings with milk of lime. About 15 litres of the oil are obtained from a cubic metre of fleece washings of 11°B. It is a slightly-coloured liquid of sp.gr. 0·835, having a penetrating smell and acrid burning taste. It consists mainly of methyl ethyl ketone (A. and P, Buisine, Compt. rend. 126, 351; 128, 561). According to Duchemin (Bull. Soc. chim. [3] 21, 798) acetone oil is of very variable composition, depending upon the nature of the pyrolignate from which it is prepared. A French Commission reported that it was effective as a denaturant of alcohol and it was adopted for this purpose by the Swiss Government in 1895.

For details of mode of manufacture from wool washings, *v.* Buisine (J. Soc. Chim. Ind. 18, 292; 21, 164); P. Baechlin, (Rev. Chim. Ind. 9, 112; 15, 240).

ACETONIC ACID *v.* HYDROXYBUTYRIC ACID.

ACETOPHENONE. *Phenyl methyl ketone.* *Hypnone* $C_6H_5 \cdot CO \cdot CH_3 \cdot$ is obtained by acting with benzoyl chloride on zinc methyl; by distilling a mixture of the calcium salts of benzoic and acetic acids; or by boiling together benzene and acetyl chloride with aluminium chloride. It can be isolated from the fraction of heavy oil of coal tar boiling at 160°–190° by addition of sulphuric acid, distilling the solution in steam and converting the distillate into the *p*-bromophenylhydrazone derivative of acetophenone (Weissgerber, Ber. 36, 754). It is best obtained synthetically by adding small quantities of sublimed ferric chloride (7 parts) to a mixture of benzene (5 parts) and acetyl chloride (7 parts) diluted with carbon disulphide. The mixture is then warmed on the water-bath, dried and fractionated (Nencki and Stoeber, Ber. 30, 1768).

Acetophenone crystallises in large plates, m.p. 20·5°; b.p. 202°. It possesses a persistent odour of oil of bitter almonds and cherry laurel water; is insoluble in water, but dissolves easily in alcohol, ether, chloroform, or benzene. It is readily oxidised by potassium permanganate to phenylglyoxylic acid (Glücksmann, Monatsh. 11, 246). By the action of ammonia on an alcoholic solution of acetophenone, the acetophenone ammonia is formed ($CMePh(N : CMePh)_3$, m.p. 115° (Thomae, Arch. Pharm. 244. 643) (*v.* KETONES).

Acetophenone forms a large number of derivatives and condensation products with aldehydes, halogens, acids, mercury salts, &c.

Acetophenone was discovered by Dujardin-Beaumetz and Bardet to possess powerful soporific properties (Compt. rend. 101, 960; Karmensky, Liss. Med. Chi. Acad. St. Petersburg, 1888–1889, No. 70). In quantities of 0·05 to 0·15 gram. it induces a quiet sleep, but is said to impart a disagreeable odour to the breath (Pharm. J. 1886, 582).

Aminoacetophenone (Camps, Arch. Pharm. 40, 15), b.p. 250°–252°; 135°/17 mm., has

anæsthetic properties, which are not diminished by condensing with aldehydes containing a phenolic hydroxyl, but are destroyed when it is condensed with benzaldehyde, tolualdehyde, or cinnamaldehyde (Hildebrandt, Chem. Zentr. 1905. ii. 502; Scholz and Huber, Ber. 37, 390; Schäfer, Ber. 39, 2181).

Isobutyracetophenone, m.p. 88°, an antipyretic substance, can be obtained by heating molecular proportions of acetophenone and *p*-phenetidene *in vacuo*, then distilling *in vacuo* at 210°–212° (Valentiner, J. Chem. Soc. Ind. 15, 50; 17, 602).

β-ACETO-PROPIONIC ACID. *Lævulic acid*

$$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H.$$
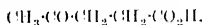
This substance is formed by the action of dilute acids on a number of carbohydrates *e.g.* levulose, inulin, galactose. It is also a product of oxidation of the terpene alcohols, but is best prepared by heating on the water-bath cane sugar with dilute hydrochloric acid (4 vols. water, 1 vol. conc. acid) until a brown flocculent precipitate is no longer formed. (Compare Tollens, Ber. 17, 668; Wehmer a. Tollens, Annalen, 243, 214.) The filtered liquid is then evaporated on the water-bath, extracted several times with ether, and after distilling off the ether the residue is fractionated in a vacuum.

It can be obtained by the hydrolysis of various nucleic acids (Kossel and Neumann, Zeitsch. physiol. Chem. 27, 2215; Inouye, *ibid.* 42, 117; Levene, *ibid.* 43, 119). For other methods of preparation, compare Tiemann and Semmler (Ber. 28, 2129); Verley (Bull. Soc. chim. [3] 17, 190); Erlenmeyer (J. pr. Chem. 179, 382); Blaise (Bull. Soc. chim. [3] 21, 617).

Lævulic acid crystallises in plates which melt at 33°. It boils at 239°, 148°–149° 15 mm. (Michael, J. pr. Chem. 152, 113), and has at 15° a sp.gr. 1·135. It is very soluble in water, alcohol, or ether, and is not attacked by bromine in the cold. Nitric acid converts it into carbon dioxide, acetic acid, succinic and oxalic acids. Iodine and sodium hydroxide form iodoform even in the cold. Hydriodic acid and phosphorus at 200° convert it into normal valeric acid; whereas sodium amalgam forms sodium γ-hydroxyvalerate acid in an alcoholic solution, and normal valeric acid in an acid solution. When added to boiling iodic acid solution diiodoacetonacrylic acid is formed (Angeli and Chiassi, Ber. 25, 2205). When placed over sulphuric acid in a vacuum it decomposes, leaving a residue of dihydroxyvaleric acid (Berthelot and André, Compt. rend. 123, 341).

The mercury salt $Hg(C_5H_7O_3)_2$, which crystallises in silvery plates, breaks up on treatment with sodium hydroxide, forming the two mercurilævulic acids $C_5H_6O_3Hg$ and $C_5H_4O_3Hg_2$. Lævulic acid readily condenses with benzil (Japp and Murray, Chem. Soc. Proc. 1896, 146), and with aldehydes (Meingast, Monatsh. 26, 265). It forms a semi-carbazone, m.p. 187° (Blaise, *l.c.*). The ethyl ester when treated with ethyl magnesium bromide yields a lactone, b.p. 105°–106°/18 mm. (Grignard, Compt. rend. 135, 627). Halogen substitution derivatives of lævulic acid have also been obtained (Wolff, Ber. 26, 2216; Wolff and Rüdel, Annalen, 294, 192; Conrad and Schmidt, Annalen, 285, 203).

The substance is employed on a manufac-

turing scale as a mordant instead of acetic acid, as it possesses the advantage of not being volatile with steam.

It is also used in the preparation of the antipyretic *antithermin*. Phenylhydrazine is dissolved in dilute acetic acid, and on adding a solution of lævulic acid a yellow precipitate is formed, which is purified by recrystallisation from alcohol (Pharm. J. [3] xvii. 801) (*v.* ANTITHERMIN).
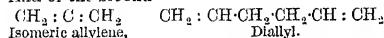
ACETOPURPURINE *v.* AZO- COLOURING MATTERS.

ACETPHENETIDENE *v.* PHENACETIN.

ACETYLENE GROUP. Hydrocarbons having the general formula C_nH_{2n-2}.

The hydrocarbons of this series exist in two isomeric modifications. Representatives of the first group are

$$CH:CH \qquad CH_3 \cdot C:CH$$
Acetylene. $\qquad$ Allylene.

And of the second

$$CH_2:C:CH_2 \qquad CH_2:CH \cdot CH_2 \cdot CH_2 \cdot CH:CH_2$$
Isomeric allylene. $\qquad$ Diallyl.

The hydrocarbons of the first group thus contain the group $\equiv CH$ united to one carbon atom, and may be designated true acetylenes. They form compounds with copper and silver in which the hydrogen of the group (CH) is replaced by the metal.

When heated to a high temperature with alcoholic potash in a sealed tube the triple bond changes its position thus:

$$C_3H_5 \cdot CH_2 \cdot C:CH \rightarrow C_3H_5 \cdot C:C \cdot CH_3.$$
$$C_2H_5 \cdot C:CH \rightarrow CH_3 \cdot C:C \cdot CH_3.$$
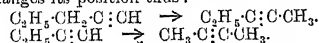
The reverse action occurs by boiling with metallic sodium.

The following general reactions yield hydrocarbons of this series :—

1. By heating the monohalogen derivatives of the hydrocarbons C_nH_{2n} with alcoholic potash

$$CH_3 \cdot CCl:CH_2 + KOH = CH_3 \cdot C:CH + KCl + H_2O.$$

2. By the action of alcoholic potash on the dihalogen derivatives of the ethylene series. In this case the reaction takes place in two stages.

I. $$CH_2Br \cdot CH_2Br + KOH$$
$$= CHBr:CH_2 + KBr + H_2O.$$
II. $$CHBr:CH_2 + KOH = CH:CH + KBr + H_2O.$$
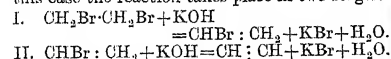
The bromine derivatives give, as a rule, a better yield than the chlorides.

3. By electrolysing unsaturated dibasic acids.
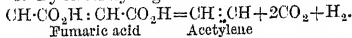
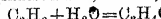$$CH \cdot CO_2H:CH \cdot CO_2H = CH:CH + 2CO_2 + H_2.$$
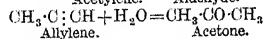Fumaric acid $\qquad$ Acetylene

The acetylenes combine with Br_2 or Br_4; thus acetylene forms $C_2H_2Br_2$ and $C_2H_2Br_4$.

Nascent hydrogen converts the acetylenes into the hydrocarbons C_nH_{2n} and C_nH_{2n+2}.

The acetylenes in presence of mercuric bromide combine with water to form aldehydes and ketones (Kutscheroff, Ber. 14, 1542; 17, 28).

$$C_2H_2 + H_2O = C_2H_4O$$
Acetylene. $\qquad$ Aldehyde.

$$CH_3 \cdot C:CH + H_2O = CH_3 \cdot CO \cdot CH_3$$
Allylene. $\qquad$ Acetone.

According to Desgrez (Ann. Chim. Phys. 1894, 3, 215; Bull. Soc. chim. [3] 11, 362), the elements of water can be made to combine directly with the acetylenes without the presence of condensing or other agents.

By polymerisation of the acetylenes, compounds of the benzene series are formed. Thus acetylene at a red heat yields benzene (Bone and Coward, Chem. Soc. Trans. 1908, 1197; Bone and Jerdan, Chem. Soc. Proc. 1901, 165; Maquenne, Compt. rend. 115, 558); allylene C_3H_4, by the action of sulphuric acid, gives mesitylene C_9H_{12} (trimethyl benzene); and crotonylene C_4H_6 gives hexamethyl benzene.

Acetylene C_2H_2 *i.e.* HC:CH is produced when an electric arc is formed between carbon points in an atmosphere of hydrogen (Bone and Jerdan, Chem. Soc. Trans. 1897, 54). Further, by passing the vapours of many carbon compounds (alcohol, ether, ethylene) through red-hot tubes (Bone and Coward, *l.c.*). It is also formed by electrolysing the sodium or potassium salt of fumaric or maleic acid, and by the action of silver, copper, or zinc-dust on iodoform (Cazeneuve, Compt. rend. 97, 1871). A steady stream of gas can be obtained by the action of the copper-zinc couple on bromoform (Cazeneuve, Compt. rend. 113, 1054).

By the action of water on the carbides of barium, calcium, or strontium (Travers, Chem. Soc. Proc. 1893, 15; Maquenne, *l.c.*; Moissan, Bull. Soc. chim. [3] 11, 1007).

By allowing the flame of a bunsen burner to strike back, or by the action of alcoholic potash on ethylene dibromide.

According to Matthews (J. Amer. Chem. Soc. 22, 106), a good laboratory method is to cover calcium carbide with absolute alcohol and add water drop by drop. The gas is purified by passing into copper sulphate solution acidulated with sulphuric acid, then over pumice stone saturated with an acetic or sulphuric acid solution of chromic acid.

Commercially acetylene is nearly always produced from calcium carbide (Lewes, J. Soc. Chem. Ind. 16, 33; Clowes, *ibid.* 209, 319; Wilson, *ibid.* 15, 103; Lüpke, Elektr. Chem. Zeit. 1895, 145; Wyatt, J. Soc. Chem. Ind. 14, 135; 796; 20, 109; Bamberger, Zeitsch. angew. Chem. 1898, 720). A rapid evolution of gas is also said to be obtained by treating calcium carbide with crystallised sodium carbonate previously mixed with powdered rock salt (J. Soc. Chem. Ind. 27, 438). Commercial acetylene often contains as impurities: ammonia, other hydrocarbons, carbon monoxide, hydrogen, nitrogen, oxygen, arsine, sulphuretted hydrogen, and phosphoretted hydrogen, the last of which is the most dangerous. The action of the gas on copper is due chiefly to these impurities. The gas can be purified and the impurities detected by passing it through cooled solutions of sulphuric acid, lime, lead or mercury salts, and chromic acid in sulphuric or acetic acid (Clowes, *l.c.*; Lunstroem, Chem. Zeit. 23, 180; Bergé and Reychler, Bull. Soc. chim. [3] 17, 218; Göttig, Ber. 32, 1879; Rossel and Landrisset, Zeit. angew. Chem. 1901, 77; Caro, J. Soc. Chem. Ind. 22, 17; 23, 15; Ullmann and Goldberg, Chem. Zentr. 1899, ii. 19; Pfeifer, J. f. Gasb. 42, 551; Frasuckel, Chem. Zentr. 1908, ii. 643; Eitner and Keppeler J. f. Gasb. 44, 548; Jaubert, J. Soc. Chem. Ind. 24, 116; Willgerodt, Ber. 28, 2107; Hoffmeister, Zeitsch. anorg. Chem. 48, 137).

The best method of freeing acetylene from phosphine is to pass the cooled gas over bleaching powder, or the compound $CaO, CaOCl_2, 2H_2O$ or $CaO, CaOCl_2, H_2O$ (Ditz, D. R. P. 1906, 162324),

moistened with just sufficient water to make it cohere in balls, and finally over lime (Lunge and Cedercreutz, Zeitsch. angew Chem. 1897, 651; J. Soc. Chem. Ind. 16, 37; 24, 1294; 27, 798; Wolff, J. f. Gasb. 1898, 41, 683).

Acetylene is a colourless gas which, when quite pure, has a distinct and agreeable ethereal odour; it has no action on metals (Clowes, J. Soc. Chem. Ind. 16, 109; Moissan, Compt. rend. 121, 566), and is non-poisonous when inhaled in small quantities, although it may produce asphyxiation when more than 40 p.c. of it is present (Clowes, *l.c.*; Korda, Mon. Sci. 45, 409; Mosso and Otto-lenghi, Ann. di Chim. e. di. Farmacol. 25, 163; Vitali, Chem. Zentr. 1898, ii. 586; Moissan, *l.c.*; Gréhaut, Compt. rend. 121, 564; Berthelot, *ibid.* 121, 566; Brociner, *ibid.* 121, 773; J. Soc. Chem. Ind. 16, 319; Rosemann, Chem. Zentr. 1895, ii. 998).

It condenses at 1° and 48 atm. to a colourless liquid which on rapid exhaustion solidifies; with water, liquid acetylene forms a crystalline hydrate $C_2H_2,6H_2O$ (Villard, Compt. rend. 120, 1262). With ozone acetylene is violently de-composed (Otto, Ann. Chim. Phys. 1898, 13, 116). It explodes more violently than other hydro-carbons with oxygen (Meyer, Ber. 27, 2764; Chatelier, Compt. rend. 121, 1144; Gréhaut, *ibid.* 122, 832; Berthelot and Vieille, *ibid.* 123, 523; Bone and Cain, Chem. Soc. Proc. 1896, 176; Clowes, J. Soc. Chem. Ind. 15, 90, 418, 701, 891).

Any mixture with air containing 3–82 p.c. of acetylene is explosive (Bunte, Ber. 31, 5; Clowes, Chem. Soc. Proc. 1896, 143; Berthelot and Vieille, Compt. rend. 128, 177), but the explosibility is reduced by admixture with inert gases. It is slightly soluble in water, more so in alcohol or ether, and very readily so in acetone, with the last three of which, according to McIntosh (J. Phys. Chem. 1907, 306), it forms crystalline compounds.

Since acetylene gas, as well as the liquid, is highly explosive under pressure, it is best stored by solution in acetone (Berthelot and Vieille, Compt. rend. 123, 523; 124, 966, 988, 996, 1000; Claude and Hess, *ibid.* 124, 626; 128, 303; J. Soc. Chem. Ind. 20, 1021, 1196; 22, 288; 24, 191, 1101; 16, 788; Wolff, Zeitsch. angew. Chem. 1898, 919; Caro, J. Soc. Chem. Ind. 25, 1138).

The gas burns in air with a smoky flame, decomposes when exposed to sunlight, and forms condensation and resinous products when sub-jected to an electric discharge (Berthelot, Bull. Soc. chim. [3] 4, 480; Jackson and Laurie, Chem. Soc. Proc. 1906, 155; Losanitsch, Monatsh. 29, 753; Javitschitsch, *ibid.* 29, 1; Cochn, Zeit. f. Elektr. 7, 681; Billitzer, Monatsh. 23, 199; Schutzenberger, Compt. rend. 110, 889).

Acetylene is now used fairly extensively for illuminating purposes, and is a safe form of artificial lighting (Lüpke, Elektr. Z. 1895, 145; J. Soc. Chem. Ind., 16, 33; 18, 476, 343; Bullier, Bull. Soc. chim. [3] 17, 646) (*v. infra*). It is used in flashing-point tests (J. Soc. Chem. Ind. 1898, 949), and has been recommended by Lunstroem for freeing alcohol from water; by Violle (Compt. rend. 122, 79), for use in photometry; by Erdmann and Makowka (Zeitsch. anal. Chem. 46, 128) for the separa-tion of copper from silver, alkaline earths,

magnesium, aluminium, chromium, manganese, iron, nickel, cobalt, bismuth, antimony, arsenic, and tin (Makowka, Zeitsch. anal. Chem. 46, 145; Erdmann, *ibid.* 46, 125; Söderbaum, Ber. 30, 760, 814, 902, 3014).

Acetylene can be used as a starting-point for the production of alcohol (J. Soc. Chem. Ind. 1900, 476; Caro, *ibid.* 1895, 226), but the methods are costly and the yield poor. Accord-ing to Vitali (L'Orosi, 21, 217), acetylene has considerable antiseptic properties.

Troubel (J. f. Gasb. 48, 1069) recommends the use of acetylene for autogenous soldering. When acetylene is burned with compressed air or oxygen in a specially adapted glass-blower's lamp, a flame can be produced but slightly luminous, which is either oxidising or quite neutral, is comparable with the electric arc in intensity, and whilst capable of melting nickel, gold, and platinum, is free from the reducing and carburetting properties of the arc (Nichols, J. Soc. Chem. Ind. 20, 29).

On heating sodium in acetylene, hydrogen is given off, and the compounds C_2HNa and C_2Na_2 are formed (Matignon, Compt. rend. 124, 775; Skosarewsky, J. Russ. Phys. Chem. Soc. 36, 863; Moissan, Compt. rend. 126, 302). With the hydrides and ammoniums of the alkali metals and of calcium, compounds of the type $C_2M'_2$, C_2H_2 are formed (Moissan, Compt. rend. 127, 911; 136, 1217, 1522; 137, 463; Berthelot and Delépine, *ibid.* 129, 361).

The compounds with copper and silver corre-spond respectively with the formulæ $C_2H_2Cu_2O$ and $C_2H_2Ag_2O$, or $C_2H_22Ag_2O$. The former is red, the latter yellowish. Both explode on heat-ing (Blochmann, Annalen 173, 174; Kuntzmann, Bull. Soc. Chem. [3] 6, 422; Alexander, Ber. 32, 238; Isolva, *ibid.* 2697; Phillips, Amer. Chem. J. 16, 340; Scheiber and Flebbe, Ber. 41, 3816; Makowka, *ibid.* 824; Freund and Mai, Chem. Zentr. 1899, i. 410; Berthelot, Compt. rend. 132, 1525).

It also forms such compounds as C_2H_2Cu,C_2Cu_2, $C_2Ag_2AgNO_3$, and more complex ones still, some of which are very explosive (Chavastelon, Compt. rend. 124, 1364; 125, 245; 126, 1810; 127, 68; 130, 1634, 1764; 131, 48; 132, 1489; Hofmann and Küspert, Zeitsch. anorg. Chem. 15, 204; Söderbaum, Ber. 30, 760, 814; Willgerodt, Ber. 28, 2107; Arth, Compt. rend. 124, 1534; Berthelot and Delépine, *l.c.*; Nieuw-land and Maguire, Amer. Chem. J. 28, 1025; Edwards and Hodgkinson, J. Soc. Chem. Ind. 23, 954; 25, 495; British Association Reports, 1904; Alexander, Ber. 32, 2381; Gooch and Baldwin, Zeitsch. anorg. Chem. 22, 235; Keiser, Amer. Chem. J. 14, 285).

Acetylene forms compounds with mercury of the type C_2Hg_2,H_2O; $3C_2Hg,H_2O$; $C_2(HgNO_2)_2$, many of which are very explosive (Nieuwald and Maguire, *l.c.*; Plimpton and Travers, Chem. Soc. Trans. 1894, 264; Keiser, *l.c.*; Plimpton, Chem. Soc. Proc. 1894, 32; Berge and Reychler, Bull. Soc. chim. [3] 17, 218; Peratoner, Gazz. chim. ital. 24, ii. 36; Gooch, *l.c.*; Alexander, *l.c.*; Hofmann, Ber. 31, 2212, 2783; Köthner, 2475; Burkard and Travers, Chem. Soc. Trans. 1902, 1270; Bilz and Mumm, Ber. 37, 4417; Brame, Chem. Soc. Trans. 1905, 427; Hofmann and Kirmreucher, Ber. 41, 314).

It also forms bromo-magnesium compounds,

$\dot{H}C$: CMgBr ; BrMgC : CMgBr (Oddo, Atti R. Acad. Lincei, 13, 187 ; Gazz. chim. ital. 38, i. 625).

With fuming sulphuric acid acetylene yields a sulphonic acid, and from the potassium salt $(C_2H_2)_3(SO_4KH)_4$ phenol can be obtained by treating with potash and distilling the product (Berthelot, Compt. rend. 127, 908 ; Schroeter, Ber. 31, 2189 ; Muthmann, *ibid.* 1880).

With fuming nitric acid, nitroform, certain neutral and acid compounds and the explosive substance $C_4H_2O_3N_4$, m.p. 78°, are obtained (Tustoni and Mascarelli, Atti Real. Acad. Lincei, 1901, 10, i. 442 ; Baschieri, Gazz. chim. ital. 31, i. 461 ; Mascarelli, *ibid.* 33, ii. 319).

With hydrogen peroxide acetylene is oxidised to acetic acid (Cross, Bevan, and Heiberg, Ber. 33, 2015).

Nascent hydrogen converts acetylene into ethylene and ethane.

When acetylene and hydrogen are passed over freshly-reduced nickel, cobalt, copper, or iron, or platinum black, ethane, ethylene, and liquid hydrocarbons are formed, in amounts depending on the nature of the metal, the relative proportions of acetylene and hydrogen, and the temperature of the reaction. When acetylene alone is passed over these metals, ethane, ethylene, hydrogen, and liquid paraffins, are formed, together with ethylenic and aromatic hydrocarbons, the proportion of the products formed depending on the catalyst and temperature. In the case of copper a greenish hydrocarbon—*cuprene* $(C_7H_6)_n$ is also formed ; a similar compound is also obtained with nickel (Sabatier and Senderens, Compt. rend. 128, 1173 ; 130, 250, 1559, 1628 ; 131, 187 ; Moreau, *ibid.* 122, 1240).

A mixture of nitrogen and acetylene subjected to the action of induction sparks yields prussic acid : $C_2H_2 + N_2 = 2HCN$ (Beilstein).

Chlorine and acetylene combine explosively when exposed to daylight, but according to Monneyrat (Compt. rend. 126, 1805), chlorine and acetylene in the absence of oxygen combine without explosion forming acetylene tetrachloride, which together with the dichloride, can also be produced by the action of acetylene on antimony pentachloride (Tompkins, D. R. P. 196324 ; J. Soc. Chem. Ind. 24, 150). The tetrachloride, which is an excellent solvent for fats, oils, and resins, can also be prepared by the action of acetylene and chlorine on acetylene dichloride when exposed to radium emanations (Lidholm, D. R. P. 1908, 201705). Acetylene can also be chlorinated by passing it into a mixture of sulphur chloride and a catalyst such as an iron compound (J. Soc. Chem. Ind. 24, 1255 ; 27, 643, 344 ; Nieuwald, Chem. Zentr. 1905, i. 1585).

Bromine added to an alcoholic solution of acetylene, or acetylene passed into bromine water, forms $C_2H_2Br_2$, but if the gas be passed through bromine the substances $C_2H_2Br_4$ and $(C_2HBr_3)_2$ are obtained (Gray, Chem. Soc. Trans. 1897, 1027 ; Elbs and Newmann, J. pr. Chem. [2] 58, 245) ; dibromoacetylene C_2Br_2, b.p. 76°–77°, is obtained by treating an alcoholic solution of tribromethylene with potash (Lemoult, Compt. rend. 136, 1333).

According to Keiser (Amer. Chem. J. 21, 261) when dry acetylene is gently warmed with solid iodine, two iodides are formed—a solid, m.p. 78°, liquid, b.p. 185° (Paternò and Peratoner, Gazz. chim. ital. 19, 580 ; 20, 670).

Acetylene diiodide $C_2I_2(C : CI_2$ Nef) is intensely poisonous (Loew, Zeit. Biol. 37, 222). According to Schenck and Litzendorff (Ber. 37, 3462), it can be used with benzene in making good photographic paper.

When subjected to the action of heat or light, C_2I_2 is changed into C_2I_4 ; with nitrous fumes it yields nitro-triiodoethylene $CI_2 : CI.NO_2$, m.p. 107° (Meyer and Pemsel, Ber. 29, 1411 ; Bilz and Werner, Ber. 30, 1200 ; 33, 2190 ; Bilz and Küppers, Ber. 37, 4412 ; Chalmot, Amer. Chem. J. 19, 877 ; Nef, Annalen, 298, 202).

Mixed halogen derivatives have also been obtained (Lemoult, *l.c.* ; Keiser, *l.c.*).

With water and carbon tetrachloride or similar halogen compounds at 0°, acetylene forms mixed crystalline hydrates (Forcrand and Thomas, Compt. rend. 125, 109).

Acetylene black, the soot produced when acetylene burns with a smoky flame or when it is exploded under two atmospheres pressure, may be used in the colour industry, calicoprinting, and also in production of ink (J. Soc. Chem. Ind. 178, 711 ; 18, 284 ; 20, 955 ; Dépierre, *ibid.* 20, 890 ; Frank, Zeitsch. angew. Chem. 1905, 1733).

Allylene or Allene C_3H_4 exists in two isomeric modifications.

1. *Methyl acetylene or allylene* $CH_3 \cdot C : CH$.

Is formed by the action of alcoholic potash on bromopropylene

$CH_3 : CBr : CH_2 + KOH$
$$= CH_3 \cdot C : CH + KBr + H_2O.$$
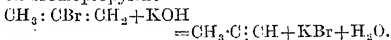
Also by acting with sodium on dichloracetone chloride

$CH_3 \cdot CCl_2 \cdot CHCl_2 + Na_4 = CH_3 \cdot C : CH + 4NaCl.$

Or by electrolysing the alkali salts of citraconic or mesaconic acids, or by action of magnesium on acetone vapour and treating the solid mass thus obtained with water (Keiser, Amer. Chem. J. 18, 328 ; Desgraz, Bull. Soc. Chem. [3] 11, 391 ; Lespieau and Chavanne, Compt. rend. 140, 1035).

Allylene is a colourless gas, b.p. $-23.5°$; m.p. $-110°$; very similar to acetylene, and, like it, forming compounds with metals. The mercuric compound $(C_3H_3)_2Hg$ is obtained by passing allylene through water containing mercuric oxide in suspension. It crystallises from hot alcohol in fine needles. It is soluble in hydrochloric acid with evolution of allylene, but does not explode on heating (Keiser, *l.c.* ; Lossen and Dorno, Annalen, 342, 187 ; Plimpton and Travers, *l.c.* ; Bilz and Mumm, *l.c.* ; Hofmann, Ber. 37, 4459).

The silver compound $(C_3H_3)_2Ag$ forms microscopic needles which explode at about 150°.

According to Berthelot (Compt. rend. 126, 561, 567, 609, 616) allylene, when subjected to the silent electric discharge, condenses to a solid with a pungent empyreumatic odour ; with nitrogen the substance $C_{15}H_{26}N$ is formed.

Allylene forms with bromine additive products, $C_3H_4Br_2$ and $C_3H_4Br_4$, and with halogen acids compounds of the type $CH_3 \cdot CCl_2 \cdot CH_3$. Concentrated sulphuric acid absorbs allylene readily and on distilling the solution with water, acetone, mesitylene, and allylenesulphonic acid

$C_3H_3SO_3H$ are formed (Schrohe, Ber. 8, 18 and 367). With hypochlorous and hypobromous acids, allylene forms dichlor- and dibrom-acetones, and trimethyl allylene yields the halogen pinacolins (Wittorf, Chem. Zeit. 23, 695).

2. *Symmetrical allylene or allene* $CH_2 : C : CH_2$ is obtained by the action of sodium on β-chlorallylchloride

$$CHCl : CH \cdot CH_2Cl + 2Na = CH_2 : C : CH_2 + 2NaCl.$$
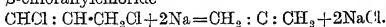
Or by the action of zinc-dust on an alcoholic solution of dibrompropylene (Gustavson and Demjanoff, J. pr. Chem. 1888, 201; Vaubel, Ber. 24, 1685; Lespieau and Chavanne, *l.c.*). And by the electrolysis of the alkali salts of itaconic acid.

The substance is a gas (b.p. $-32°$; m.p. $-146°$), but differs from unsymmetrical allylene in giving no precipitate with an ammoniacal copper or silver solution (Phillips, Amer. Chem. J. 16, 340). With aqueous mercuric chloride allene and its homologues yield white precipitates (Vaubel, *l.c.*; Lossen and Dorno, *l.c.*). It unites with bromine to form $C_3H_4Br_4$, b.p. 225°–230°, with decomposition.

According to Smirnoff (J. Russ. Phys. Chem. Soc. 35, 854; 36, 1184), the allene hydrocarbons can be identified by treatment with hypochlorous acid, when keto-alcohols of distinctive properties are obtained.

Butines C_4H_6.

Four isomerides exist.

1. *Ethylacetylene* $C_2H_5 \cdot C : CH$. Formed by the action of alcoholic potash on $C_2H_5 \cdot CCl_2 \cdot CH_3$ (Bruylants, Ber. 8, 412).

By passing acetylene and ethylene through a red-hot tube (Berthelot, Ann. Chim. Phys. [4] 9, 466).

The compound is a liquid boiling at 18°, and is a true acetylene, since it forms precipitates with ammoniacal copper and silver solutions. With ammoniacal silver chloride and alcoholic silver nitrate it forms explosive compounds (Wislicenus and Schmidt, Annalen, 313, 221); it also yields a sodium derivative (Jociez, Chem. Zentr. 1897, i. 1012).

2. *Crotonylene* or *dimethylacetylene*

$$CH_3 \cdot C : C \cdot CH_3,$$
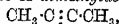
Formed by acting with alcoholic potash on βγ-dibromobutane $CH_3 \cdot CHBr \cdot CHBr \cdot CH_3$; by the action of sodium ethoxide on monobrompseudo-butylene MeCBr : CH·CMe (Hölz, Annalen, 250, 230); or by the decomposition of the salts of β-bromoangelic acid (Wislicenus, Talbot, and Henge, Annalen, 313, 228). It is a liquid, b.p. 27·2°–27·6° (Wislicenus and Schmidt, *l.c.*). With bromine it forms a liquid $C_4H_6Br_2$, b.p. 146°–147° (Hölz, *l.c.*), and $C_4H_6Br_4$, which is solid, m.p. 243°; *iso*crotonylene dibromide, b.p. 149°–150°, is also known, and is not readily attacked by zinc-dust (Wislicenus and Schmidt, *l.c.*).

Crotonylic mono- and hydro-bromides, as well as the iodide and chloride derivatives, have also been obtained (Wislicenus, Talbot, and Henge, *l.c.*; Peratoner, Gazz. chim. ital. 22, ii. 86; Charon, Ann. Chim. Phys. 1899, 17, 228; Favorsky, J. pr. Chem. [2] 42, 143).

On shaking the hydrocarbon with sulphuric acid and water (3:1), hexamethylbenzene is obtained

$$3C_4H_6 = C_{12}H_{18} = C_6(CH_3)_6.$$
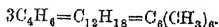
3. *Vinyl-ethylene* $CH_2 : CH \cdot CH : CH_2$ (Perkin and Simonsen, Chem. Soc. Trans. 1905, 857). Prepared by passing the vapours of fusel oil through a red-hot tube (Caventou, Annalen, 127, 348). It is present in compressed coal gas (Caventou, Ber. 6, 70), and in oil gas (Armstrong and Miller, Chem. Soc. Trans. 1886, 74). It gives no precipitate with an ammoniacal cuprous chloride solution. When treated with bromine in chloroform solution cooled to $-21°$, it gives a liquid dibromide, b.p. 74°–76° /26 mm., which at 100° is converted to a solid of the same composition, m.p. 53°–54°, b.p. 92°–93° /15 mm.; with bromine the liquid dibromide yields a tetra-bromide (Griner, Compt. rend. 116, 273; 117, 553; Thiele, Annalen, 308, 333).

4. The *butine* $CH_3 \cdot CH : C : CH_2$ is prepared by heating tetrachlorbutane with alcohol and the zinc-copper couple; or from chloral by treatment in the cold with zinc ethyl. It is a colourless liquid, b.p. 18°–19°, yields no precipitate with ammoniacal copper solutions, but with bromine yields di- and tetra-bromine derivatives (Norton and Noyes, Amer. Chem. J. 10, 430).

The compound $CH : CCl : CH$, formed by the action of cupric chloride on copper acetylene, is described by Noyes and Tucker (Amer. Chem. J. 19, 123); pentachlorbutine C_4HCl_5 by Zincke and Kuster (Ber. 26, 2104).
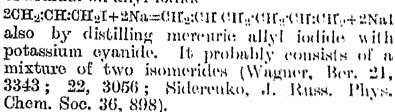
Derivatives of the butines, some of which are used as dye-stuffs, are described by Freund (Ber. 34, 3109).

Pentines. Seven of eight possible pentines are known, of which *isoprene* obtained in the dry distillation of indiarubber is the most important (Ipatieff and Wittorff, J. pr. Chem. [2] 55, 1; Ipatieff, *ibid.* 4). It can be obtained synthetically by the action of alcoholic potash on β-dimethyltrimethylene dibromide. It has b.p. 33°–34°, unites with hydrogen bromide forming $CMe_2Br \cdot CH_2 \cdot CH_2Br$, and has no action on ammoniacal cuprous chloride or silver nitrate (Euler, J. pr. Chem. [2] 57, 131).

When saturated with hydrogen chloride at 0° and then allowed to remain in a sealed tube at the ordinary temperature for two or three weeks, a substance analogous to indiarubber is formed (Bouchardt, J. Soc. Chem. Ind. 21, 56).

Two trimethylene pentines and *cyclo*pentine have also been obtained.

Of the higher terms of the series the *hexine diallyl* is of interest. It is formed by the action of sodium on allyl iodide

$$2CH_2 \cdot CH \cdot CH_2I + 2Na = CH_2 \cdot CH \cdot CH_2 \cdot CH : CH \cdot CH_2 + 2NaI$$

also by distilling mercuric allyl iodide with potassium cyanide. It probably consists of a mixture of two isomerides (Wagner, Ber. 21, 3343; 22, 3056; Siderenko, J. Russ. Phys. Chem. Soc. 36, 898).

It forms a liquid smelling of horse-radish, boiling at 59°, and combines with bromine to form the tetrabromide $C_6H_{10}Br_4$, melting at 63°. If this be boiled with potash a liquid dibromo-diallyl is obtained, which boils at 210°, and by the action of alcoholic potash yields *dipropargyl* C_6H_6, a liquid boiling at 85° isomeric with benzene, but having the constitution

$$CH : C \cdot CH_2 \cdot CH_2 \cdot C : CH.$$
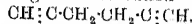
ACETYLENE AS AN ILLUMINANT. Although acetylene was discovered by Davy as far back as 1836, its use as an illuminant became

practicable only in 1892, when Moissan in France, and T. L. Willson at Spray, showed that it was possible to make calcium carbide on a commercial scale in the electric furnace.

At temperatures above 3000° a mixture of lime and some form of carbon, such as coke, soot, anthracite, or charcoal, becomes semi-liquid, and reduction of the calcium oxide results with production of carbon monoxide and liberation of calcium, which unites with the excess of carbon to form calcium carbide :

$$2CaO + 3C_2 = 2CO + 2CaC_2$$
Lime.   Carbon. Carbon monoxide. Calcium carbide.
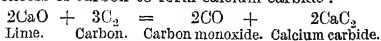
Water decomposes the carbide with reproduction of lime and generation of acetylene :

$$CaC_2 + H_2O = CaO + C_2H_2$$
Calcium carbide. Water.   Lime.   Acetylene.
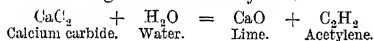
In the early days of carbide manufacture little attention was paid to the purity of the materials, with the result that the compound formed contained impurities, some of which were decomposed by water and gave products contaminating the acetylene. Since the importance of purity in the acetylene has been recognised, everything possible is now done to reduce such impurities to a minimum.

The lime employed is burnt in special kilns heated by gas, as the ordinary method of lime-burning by means of coal, &c., introduces so many impurities into the finished material that a bad carbide results. The limestone from which the lime is obtained must be as free from foreign matter as possible for the same reason. The same restriction applies to the carbonaceous matter used as the source of the carbon, and it is of the utmost importance that the ash, sulphur, and phosphorus should be as low in quantity as possible.

The proportions of the lime and carbon required by theory are 56 parts of lime to 36 parts of carbon, but allowance has to be made for impurities and loss in manufacture, so that the ratio now adopted is 100 of lime to 70 of carbon, whilst in some cases, to ensure a more fusible product, a rather higher proportion of lime is used, but the carbide so made has a slightly inferior gas-generating power.

Various types of electric furnace have been devised for the manufacture of calcium carbide, but they can be divided practically into two classes : (a) those in which the arc is struck in a mass of the mixed lime and carbon placed round the poles, the upper pole being raised as the carbide is produced, thus gradually building up an 'ingot'; and (b) those in which the mixture is fed continuously between the carbon poles, the carbide remaining in the furnace in a fused condition, and being tapped from time to time, the product being known as 'run' carbide.

At the present time nearly all the European carbide is made by the latter process, whilst ingot carbide is still largely made in America, a rotary furnace of the 'Horry' type being much used, in which the slow revolution of the furnace removes the ingot as it is formed from the direct impact of the arc, and presents a fresh portion of the charge to its action.

For all practical purposes it may be stated that 1 E.h.p. per year will yield one ton of carbide. The size of the furnace in the case of the 'run' carbide is limited only by the size of the carbon electrodes that can be obtained ; with 'ingot' carbide a furnace taking about 200 E.h.p. is the most useful, taking into consideration efficiency as well as wear and tear. The most usual current for such a furnace would be about 12 to 15 amperes per square inch of electrode surface at a pressure of 55–65 volts.

Cheap power is of course the main factor in the economical production of calcium carbide, and this has resulted in the carbide industry becoming localised in those districts where water power is available, but the important advances which have of late taken place in the development of power from gaseous fuel will probably result in the establishment of factories in localities where the necessary material can be readily obtained and a local market secured for the product, since carriage necessarily influences the cost of production.

The cost of production of calcium carbide may be taken as being about 7l. per ton under the most advantageous conditions.

Calcium carbide, as made in the electric furnace, is a dark crystalline substance with a metallic lustre, having a density of 2·22. The pure compound, however, has been produced by Moissan in thin white semi-transparent plates, the colour of the commercial material being due to the presence of iron and other impurities.

The impurities found in commercial carbide may be divided into those which can be decomposed by water, and those on which water has no action. Amongst the former are substances evolving phosphorus compounds on contact with water, aluminium sulphide, organic sulphur compounds and metallic nitrides : whilst the latter class contains such bodies as graphite, carbides of boron and silicon, carbides and silicides of various metals contained in the lime and in the ash of coke, these being left with the lime residue after the decomposition of the carbide by water, and in no way influencing the purity of the gas.

The purity of commercial acetylene depends primarily on the purity of the carbide from which it is generated, and as long as it is impossible to get absolutely pure materials for the manufacture of the carbide, so long will impurities be found in the gas made from it. The most important of these impurities are :

(a) Phosphoretted hydrogen, obtained from the decomposition of calcium phosphide, &c., by water, and, in burning with the acetylene, gives rise to phosphorus pentoxide, which forms a light haze in the room in which the gas is being burnt.

(b) Sulphuretted hydrogen, formed by the action of water on aluminium sulphide, &c., and yielding when burnt sulphur dioxide, which if dissolved by condensing moisture will absorb oxygen from the atmosphere, forming traces of sulphuric acid.

(c) Ammonia, from the magnesium nitride, which rapidly corrodes brass gas-fittings, and on burning produces traces of nitrogen acids.

Siliciuretted hydrogen is also found in small quantities in crude acetylene.

Several processes have been devised for the purification of acetylene by the removal of these compounds as well as of the hydrocarbon vapours formed by the polymerisation of the gas due to high temperature during generation.

The only impurity that offers any real difficulty in removal is the phosphoretted hydrogen, and three substances have been suggested and used in practice for this purpose: (a) bleaching powder, (b) acid copper or iron salts, and (c) acid solution of chromic acid.

The bleaching powder is employed in the form of small lumps, as offering the least resistance to the flow of the gas when in a slightly moistened state. Its action is purely that of oxidation, the phosphoretted and sulphuretted hydrogen being converted respectively into phosphoric and sulphuric acids, the acetylene being unaffected. To obtain as large a surface as possible the bleaching powder is sometimes mixed with an inert body, such as sawdust or oxide of iron, but in whatever condition the bleaching powder is used the gas requires an after-purification for the elimination of chlorine compounds, for which purpose a lime purifier is generally employed.

Bleaching powder, though an efficient purifying agent when in good order, is apt to be uncertain in its action, and cases have frequently occurred of spontaneous firing and explosion when air has been admitted to purifiers containing this material that have been in use for some time, so that precautions are necessary when using this method of purification.
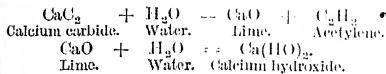
An acid solution of cuprous chloride, or solids made by impregnating kieselgühr or similar porous bodies with the acid copper salt, are also very effective in removing the various impurities, the phosphorus and sulphur compounds being transformed into copper phosphide and sulphide. The disadvantages of the process are that a second purification with lime is required to remove acid vapours, and that the material being highly acid cannot be used in ordinary metal containers, whilst if the copper salt became neutralised by ammonia there might be danger of the explosive copper acetylide being formed. Under suitable conditions 1 kilogram of the material will purify 20 to 25 cubic metres of the gas, the acetylene not being acted upon, and the action being regular and certain.

Chromic acid in solution containing sulphuric or acetic acid, or kieselgühr charged with this mixture, is the third purifying agent, and eliminates the phosphoretted and sulphuretted hydrogen and the ammonia. When exhausted the spent material can be regenerated by exposure to the air.

In practice these three materials seem to give equally good results, and the passage of the gas through the solution or solid scrubs out of it to a great extent the tarry fog and lime dust often mechanically held in the gas when it has been generated too rapidly or at too high a temperature.

Absolute purification is by no means necessary; for ordinary use all that is required being to reduce the amount of impurity below the limit at which the products of combustion are injurious to health or cause haze; and with a fairly pure specimen of carbide mechanical scrubbing is sufficient if a generator of the non-automatic type is employed, and the gas is stored in a holder before use.

When calcium carbide is acted upon by water the changes that take place may be represented by the equations :—

$$CaC_2 \quad + \quad H_2O \quad = \quad CaO \quad + \quad C_2H_2$$
Calcium carbide.   Water.   Lime.   Acetylene.

$$CaO \quad + \quad H_2O \quad = \quad Ca(HO)_2.$$
Lime.   Water.   Calcium hydroxide.

And so great is the affinity of the carbide for water that the calcium hydroxide so formed is slowly decomposed on standing by any excess of the carbide.

The first generator was of the simplest construction, the carbide being contained in a glazed vessel provided with two side tubulures and a lid that could be clamped down gas-tight. Through one of the tubulures water was admitted by means of a siphon, whilst the gas evolved was led through the other tubulure to a holder, but when the commercial possibilities of the gas had become apparent, inventors at once turned their attention to the multiplication of the forms of generator.

Although the generation of acetylene by thus bringing calcium carbide in contact with water seems so simple, yet in actual practice it was complicated by several difficulties, amongst which may be mentioned the heat of the reaction, which caused the polymerisation of some of the acetylene, and by the fact that the evolution of gas did not cease immediately the water supply was cut off, this being due to water mechanically held in the residue formed, to the dehydration of the calcium hydroxide by the unchanged carbide, as well as to the moisture condensed from the gas as the temperature of the generator fell.

Acetylene generators can be divided into two main classes—those in which water is brought in contact with the carbide, the latter being in excess; and those in which the carbide is thrown into water, the water being always in excess. The first class may be subdivided into those in which water is allowed to rise to the carbide, those in which it drips on to the carbide, and those in which a vessel full of carbide is lowered into water and then withdrawn as the generation of the gas becomes excessive.

Each of these types may be 'automatic' or 'non-automatic.' In the former are to be found devices for regulating and stopping at will the generation of the gas within limits, whilst the 'non-automatic' variety aim at developing the gas from the carbide with as little loss as possible and storing it in a holder.

The points to be aimed at in a good generator are :

(a) Low temperature of generation.

(b) Complete decomposition of the carbide.

(c) Maximum evolution of gas from carbide used.

(d) Low pressure in every part of the apparatus.

(e) Removal of all air from the apparatus before collection of the gas.

Generators of the 'drip' type, in which water is allowed to fall slowly upon a mass of carbide, possess most of the disadvantages due to heat of generation, fluctuation of pressure, &c., and this type has been abandoned except for the smallest forms of portable generator. Those in which water rises to the carbide are most efficient, and overheating can be avoided by ensuring that the water never rises above that portion of the carbide which is undergoing decomposition : in other words, that the gas

leaves the carbide immediately upon its formation and passes away to the holder with the least opportunity for becoming overheated by contact with decomposing carbide.

Generators in which the carbide dips into water and is then withdrawn are apt to overheat to a dangerous extent, especially if the generator be over-driven.

Although it might be expected that the dropping of the carbide into an excess of water would produce the coolest and purest gas, yet this is not the fact, and evidence of over-heating of the gas is often found in generators of this class, as a coating of lime can form around the lumps, preventing the free access of water, and allowing the interior of the mass from which generation is proceeding to become heated to redness; the efficiency also is very low, as a considerable amount of the gas is dissolved in its upward passage through the large volume of water.

Theoretically 64 parts by weight of carbide require only 36 parts by weight of water for complete decomposition and conversion of the lime into hydroxide, but it is found in practice that, owing to the heat of the reaction driving off some of the water as steam, and a further portion mechanically adhering to the slaked lime, double this amount of water is necessary, and the only safe way to ensure entire decomposition of the carbide is to add sufficient water to flood the residue.

When acetylene is burnt in air under such conditions as to complete its combustion, it is converted into carbon dioxide and water vapour, the same compounds that are produced by all combustible hydrocarbons, 1 cubic foot of the gas requiring $2\frac{1}{2}$ cubic feet of oxygen, or five times that amount of air.

When acetylene was first used for illuminating purposes, Bray union jet burners were employed, and although a very high duty was obtained, the pressures necessitated were too high to be desirable, and carbon was rapidly deposited on the burner tip, and caused such serious smoking of the flame as to considerably prejudice the use of the new illuminant. The proper combustion of any hydrocarbon gas, however rich in carbon, can be effected by supplying the flame with exactly the amount of air necessary to prevent smoking, and it is under these conditions that the highest illuminating effect possible with a particular burner is obtained. The ratio between the air to be supplied and the gas consumed depends upon the thickness of the flame and the pressure at which the gas issues from the burner.

If acetylene be burnt from a 000 Bray union jet burner at ordinary pressure a smoky flame is obtained, but if the pressure be increased to 4 inches an intensely brilliant flame results, free from smoke and giving an illuminating value of 240 candles per 5 cubic feet of gas consumed. For practical purposes, however, this pressure is too high, and the largest burners at first adopted, which required the consumption of 1 cubic foot of acetylene per hour, gave on an average 32 candles at an inch pressure.

These first burners were of the union jet type, in which very fine holes were employed for the delivery of the gas, and drilled at a more obtuse angle than ordinarily used for coal gas, thus causing a greater insuck of air into the flame, and ensuring a more complete combustion. Some specially small union jet burners were also produced by Bray, and both these nipples answered extremely well for a time and developed from 30 to 36 candle power per cubic foot of gas consumed, but they both had the same weakness, and after a few hundred hours began to smoke, and evolve copious clouds of soot-flakes.

This trouble generally began by a filiform growth of carbon appearing on the jet of the burner, which quickly distorted the flame, impeding proper combustion and causing the formation of quantities of free carbon. If the burner was cleaned and relighted, the trouble began again in an hour or two, and the only remedy was to replace the burner by a new one.

The smoking of acetylene burners after they have been in use for some little time, more particularly if the gas be turned down, is due indirectly to the property possessed by acetylene, in common with many heavy gaseous hydrocarbon compounds, of polymerising as the temperature rises; and also to the pressure at the burner-tip being insufficient to impart to the gas the velocity necessary to ensure the admixture with sufficient oxygen to effect its complete combustion; or, in some cases to the flow of gas through the burner holes being checked by accumulation of foreign matter therein.

If the steatite jet of a burner in which smoking has developed be broken it will be found to be carbonised for some depth into the material, showing that a liquid hydrocarbon has soaked into the steatite and has been decomposed by heat with deposition of carbon. The generally accepted idea is that the heat of the burner polymerised some of the acetylene to benzene, and that this scrubbed out by friction at the nipple led to the carbonisation and choking of the burner. Another theory, however, is that the heat evolved by the reaction between the carbide and water in the generation of the gas polymerises some of the acetylene immediately upon its formation, and that a certain quantity of the liquid hydrocarbon so formed is held in suspension and carried by the gas as a vapour to the burner, where it is scrubbed out by frictional contact and gradually accumulates there and is decomposed.

Although the deposition of carbonaceous matter does not take place so readily in burners supplied with gas that has been generated slowly and at a low temperature with subsequent washing and purification, yet it is a fact that the trouble arises when the gas is in the purest possible condition. Gas generated below 280° will not so frequently give rise to the trouble of carbonising at the burner, but if this temperature be exceeded in generation, no after-treatment of the gas will prevent it.

A small percentage of water carried along with the gas mechanically, or a little lime dust held in suspension, is also a source of carbon deposit at the burner.

Carbonisation of the burner is aggravated by 'turning down,' in which case the flow of gas is checked and the flame plays about the tip of the burner, heating it to a temperature favourable to polymerisation, when carbon is deposited, and by its catalytic action causes the

accumulation of further growths. If, however, the gas is burned at full pressure, the flame is not in actual contact with the burner, and the velocity of the issuing jet of gas induces currents of air around and through it, which prevent the temperature of the burner being raised to a degree sufficient to polymerise the gas to any material extent.

For the above reasons it was soon discovered that ordinary gas burners of the union jet pattern were unsuitable, although attempts had been made in America to use acetylene diluted with a certain proportion of air, which permitted it to be burnt in flat flame burners, but the danger of such admixture being recognised efforts in this direction were soon abandoned.

In France burners were devised in which jets of acetylene coming from two tubes spaced some little distance apart were made to impinge and splay each other out into a flat flame, whilst soon after Bullier introduced the idea of sucking air into the flame at or just below the burner-tip.

No real advance, however, was made in burners for acetylene until 1896–97, when Bullier's principle of making the tips of the burner jets into small bunsens was adopted by Dolan in America, and Billwiller on the Continent.

The Billwiller burner has two steatite arms rising at right angles from a common base from which the acetylene issued at two small orifices exactly opposite each other and giving the double jet. Immediately above the gas orifice a small platinum plate was fixed at a distance of about 0·5 mm. from the steatite, with a hole in it rather larger than the orifice in the steatite just below. The acetylene issuing from the hole in the steatite rushed through the hole in the platinum above and drew air in under the platinum plate. The air so drawn in flowed to the confines of the rapidly travelling stream of acetylene and passed upwards around it, so preventing contact between the edge of the hole in the platinum and the acetylene, whilst the metal, being part of a collar of platinum fixed round each steatite arm, and being a good conductor of heat, prevented such heating as would lead to the deposition of carbon from the gas.

Fig. 1.

These burners, made by Schwarz of Nuremberg, and sold under the name of the 'Basle' burner, gave excellent results, as is shown in the following table :—

Number of burner	Gas consumed (cub. ft.)	Pressure in inches (water)	Total light (candles)	Candles per cub. ft. of gas
1	0·35	2·25	4·2	12·0
2	0·625	2·25	19·0	30·4
3	0·75	3·0	24·0	32·0
4	0·90	3·0	32·0	35·5
5	1·00	3·0	36·0	36·0
6	1·00	3·0	40·0	40·0

In 1897 Dolan in America made a burner on the same principle as the Billwiller burner,

though of slightly different construction. It consisted of a metal base, the upright from which forked into two arms, which near their extremities were bent inwards at right angles. These arms carried steatite or 'lava' tips, bored with a fine hole from the interior to the base of the mushroom head, where its diameter was more than doubled, whilst four small lateral air tubes were bored at regular intervals from the base of the head to the broad aperture of the nipple, with the result that the flow of acetylene from the narrow into the wider tube sucked air in through the side tubes and surrounded the ascending gas with an envelope which prevented its contact with the heated tip. These burners, which are more generally known as the 'Naphey' burners, gave very good results, and have been more widely adopted than the Billwiller burners that preceded them, partly because they did away with the expense of the platinum, were cheaper to make, and were less liable to break.

These tips were very largely manufactured on the Continent, both the American and English supply coming from Nuremberg. The form of mounting, however, was considerably varied in order to suit the taste of the user or to give the burner a new name. In one very popular form the arms are made as a portion of a circle, this modification doing away with the friction and check to the flow of gas due to the sharp bend in the original pattern, whilst these again are made up in groups of two or three burners where greater illumination is required.

The great drawback to all the Naphey tip burners is that the heat from the flame causes a slight and gradual warping of the metal mounting, with the result that after a time the jets become slightly thrown out of their true position, which at once distorts the flame and causes it to throw up smoky points. This trouble is not found with burners having steatite or composition arms, as these, being pressed or cut, do not warp with the heat.

These burners proved the forerunner of a host of others in all of which the same principle was adopted, one of the simplest and most popular being shown in Fig. 2, whilst Fig. 3 is a section
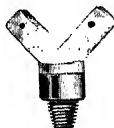

Fig. 2.   Fig. 3.

of the same burner, showing the construction and air inlets.

Although these burners possess many advantages and can be used for several hundred hours without smoking, they have the drawback that the flame cannot be turned down, as, after the flame has been left turned down for an hour or two, it will be found that it will generally start smoking when the normal consumption is restored.

In order to overcome this trouble Bray introduced a burner in which, by placing a second air-supply chamber of larger dimensions above the first, such a complete encircling of the jet of gas by air was ensured that the variations

in gas pressure caused by turning down the flame do not lead to carbonisation.

The same principle is utilised by Schwarz in the ' Suprema ' burner made at Nuremberg, which is shown in Fig. 4.

Another burner has been brought out by this maker in which the idea of air injection has been successfully adapted to a slit burner: the gas issues from a series of fine holes placed below a cap provided with a broad slit
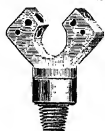
FIG. 4.   FIG. 5.

and side air tubulure, the gas drawing in sufficient air in its passage through the slit to prevent smoking or carbonisation of the burner (Fig. 5).

From the earliest introduction of acetylene attempts have been made to utilise it with incandescent mantles, but under the pressures which are usually obtained from the ordinary generating apparatus this has not proved successful. Acetylene, when consumed in an atmospheric burner, gives an excessively hot flame, not only on account of its composition, but also from its endothermic character. Several difficulties, however, are met with in trying to burn acetylene mixed with air in sufficient proportion to yield a non-luminous flame, namely :

(a) The wide range over which such mixtures are explosive.

(b) The low temperature of ignition.

(c) The high speed at which the explosive wave travels through the mixture of gas and air.

In order to make a bunsen burner for acetylene the tube has to be very narrow, and even then flashing back is very liable to occur, whilst a high pressure is needed to bring about a satisfactory mixture of the gas with sufficient air to ensure combustion with an absolutely non-luminous flame. The range of explosibility lies between 3 p.c. and 82 p.c. of acetylene in the mixture, and the propagation of the explosive wave cannot be stopped by the ordinary device of using wire gauze, on account of the low ignition point of the mixtures. By using a tube ½ mm. in diameter the explosion ceases to be propagated at all, but such tubes, on account of their small diameter, cannot be utilised singly. The difficulty can be surmounted by using a bundle of small tubes united to form a single burner, or by employing a large tube having a constriction at one point of not more than 5 mm. diameter. The diameter of the tube at the constriction must be in a definite proportion to the particular mixture of air and acetylene consumed, as the more air the greater must be the constriction in the strangulated portion of the tube, owing to the increased velocity of the explosive wave.

With an acetylene bunsen, and using a Welsbach No. 2 mantle, as much as 90 candles per cubic foot of acetylene has been obtained. It may be taken that when used with a mantle acetylene will give double the illuminating power per cubic foot as compared with the light obtained when the gas is burnt in the ordinary

acetylene flat-flame burners under the best conditions, but very widely different results have been obtained, owing to irregularities in the pressure or lack of air regulation, and at the moment of lighting or turning out there is a liability of a small but violent explosion, which has disastrous effects upon the mantle. A further difficulty is caused when phosphoretted hydrogen is present as an impurity, for this leads to the formation of fusible phosphates of thorium and cerium, with consequent destruction of the mantle. Apart from these considerations, the mantle appears to be hardened and strengthened by the intense heat to which it is subjected, but it is not yet determined how the life of the mantle is affected by the temperature of the flame.

Under the light yielded by the combustion of acetylene colours appear practically the same as in daylight, and all tints and shades can be as clearly distinguished from one another as in sunlight. For this reason the gas has been found to be of invaluable utility in dyeing and colour printing. The spectrum of acetylene, however, although the same as that of daylight for red and yellow, has an increase in the blue rays of 0·46, which brings them to about the same value as the Northern Light. The violet rays show a slight increase, so that acetylene is even richer than sunlight in the rays which are so essential to the chemical action of light, and yet the red rays which are so detrimental in colour work do not predominate, as in the electric arc.

In 1896 Claude and Hess, in France, suggested the idea of making use of the solubility of acetylene in certain liquids as a means of storing this gas, and acetone was tried as the solvent. But it was found that the simple solution of acetylene in acetone, although less liable than the compressed or liquefied acetylene to explosion, could not be said to be sufficiently free from danger to admit of its general use. It was soon discovered by Janet and Fouche that when acetylene is dissolved in acetone absorbed by porous material of the right kind under 10 atmospheres pressure, it was impossible to produce explosion. The medium employed has a porosity of 80 p.c. soaked with 43 p.c. of the capacity of the cylinder with acetone. In this way one cubic foot of cylinder space can be made to hold 100 cubic feet of acetylene, which is, to a large extent, given off when the tap of the cylinder is opened.

Acetone dissolves 24 times its volume of acetylene at 15° and under ordinary atmospheric pressure, the solubility increasing with the augmentation of pressure, and the volume of the acetone also increasing very largely. Under 12 atmospheres 300 volumes of gas are dissolved.

The oxy-acetylene flame has within the last few years become of great service in autogenous welding. The advantages of such a flame were well recognised previous to 1901, but considerable difficulty was experienced in providing a blowpipe which would consume the acetylene at low pressures, and it was not until the introduction of dissolved acetylene that success was attained. Blowpipes are now made in which the oxygen alone is under pressure, the acetylene being under the low pressure as

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delivered from a generator. The two systems are known as the high-pressure and low-pressure methods of oxy-acetylene welding.

The temperature of the oxy-acetylene flame is approximately 3000°, and from the nature of the combustion the flame has a reducing action tending to exclude the possibility of oxidation of the metals undergoing treatment. Theoretically 2·5 volumes of oxygen are required for each volume of acetylene, but in practice it is found that the proportions are approximately 1·4 to 1·0, this low proportion of oxygen ensuring a reducing action in the flame.

In the high-pressure system the oxygen is delivered from an ordinary cylinder under pressure, and the acetylene, dissolved in acetone under pressure, is also supplied from cylinders. Both cylinders are fitted with special governors, as a perfect regulation of the flame is one of the main secrets of success.

With the low-pressure plant the acetylene is made in an ordinary generator, which may be of the automatic or non-automatic type, the size of the works to a great extent influencing the kind of generator used, but, whatever type be adopted, it is necessary that the generation of the gas should not be accompanied by overheating, as this leads to low temperatures at the burner and other troubles. The gas should be purified before use, as the presence of the phosphoretted and sulphuretted hydrogen would tend to spoil the weld, and the purifying agent should be renewed when necessary. After leaving the purifiers the gas is distributed to the various points in the workshops in gas- or steam-barrel piping, and at each point a hydraulic back-pressure valve is inserted, in order to prevent the oxygen through any mischance flowing back through the acetylene service. The first successful blowpipe was the Fouche, employed with the low-pressure system, and this type has held its own in spite of the competition of other patterns. After the weld has been made the plate is annealed, this being essential. Although the results of tests up to the present are not very consistent, it may be taken that, on the average, the welded joint has a tensile strength from 95 to 80 p.c., depending on the thickness of the plate.

There are many classes of work in which oxy-acetylene welding can be advantageously employed. In the motor-car industry, both in the garage and repair shop, it has proved of great service, it being a comparatively simple matter, for instance, to mend a cracked cylinder or gear-box. For the welding of tubes, repairs to boilers *in situ* needed by corrosion, &c., for the mending of fractured stems and stern posts, the process has been invaluable.

Acetylene has been found of great service in the illumination of small towns and country villages, and for isolated houses and farms. It has been employed in photography on account of its richness in actinic rays. For headlights on motors, for train lighting, for buoys, and in fact in a number of cases where bright and trustworthy light is required without the complication of a coal-gas works or the dangers of oil, acetylene has proved its worth.

It has been found that the rays from an acetylene light possess remarkable penetrative powers in fog or mist, being in this respect superior to the arc light or incandescent mantle.
    V. B. L.

ACHRODEXTRIN *v.* DEXTRIN.

ACHYRANTHES ASPERA or *Aghara*. An Indian plant used as a simple and as a remedy for toothache.

ACID ALBUMEN *v.* PROTEINS.

ACID ALIZARIN, -BLUE. -GREEN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ACID CERISE *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACID GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACIDIMETRY and ALKALIMETRY. This branch of quantitative analysis dealing with the estimation of acids and alkalis is of great technical importance. In pure aqueous solutions the amount of acid or alkali can usually be ascertained with considerable accuracy by determining the specific gravity of the liquid at a definite temperature and referring to a table especially drawn up for this purpose.

Direct estimations may also be made by suitable gravimetric methods, but volumetric processes are almost exclusively employed, and are indeed the only methods available for distinguishing between free and combined acid or alkali. In these operations the quantity of acid or alkali present is calculated from the amount of standard alkali or acid required respectively to neutralise it exactly, the precise point of neutralisation being determined by the addition of a small quantity of an *indicator*, *i.e.* a substance which by undergoing a marked change of colour renders evident the transition from acidity to alkalinity, or *vice versa*.

Indicators. Although many natural and artificial colouring matters have been recommended as indicators, comparatively few are actually used, those most frequently employed being *methyl orange*, *phenolphthalein*, and *litmus*.

Artificial indicators are either very weak organic acids or (more rarely) weak bases, and the prevalent view regarding their behaviour is that in solution their colour in the non-ionised state differs from that which they exhibit in the ionic condition.

In accordance with the ionic theory of solution, a very weak acid HM exists in solution, mainly, but not entirely, in the non-ionised state, the equilibrium between ions and undissociated molecules $HM \rightleftharpoons \overset{+}{H} + \overset{-}{M}$ being expressed quantitatively by the equation

$$\overset{-}{M} \times \overset{+}{H} / HM = \text{constant}$$

in which the symbols denote the molecular concentrations of the ions and molecules, and where as in the case under discussion $\overset{--}{M}$ and $\overset{++}{H}$ are very small in comparison with HM.

Any increase in the value of $\overset{+}{H}$, which is effected by adding a small quantity of a fairly strong (ionised) acid to the solution, leads to a corresponding diminution in the value of $\overset{-}{M}$. The reverse change, leading to an increase in the value of $\overset{-}{M}$, with a corresponding decrease in the value of $\overset{+}{H}$, is effected by adding a slight amount of a fairly strong (ionised) alkali hy-

droxide, since the equilibrium $\overset{+}{H} \times \overset{-}{OH} = $ constant obtains in aqueous solutions, and the alkali added increases considerably the value of the factor $\overset{-}{OH}$. If the acid HM and the ion M differ in colour, then, in any solution containing this acid a change from acidity to alkalinity, *i.e.* from a state in which $\overset{+}{H}$ predominates over $\overset{-}{OH}$ to the reverse condition, may be indicated by an appreciable change of colour. The degree of ionic dissociation of the indicator HM must, however, be considerably smaller than that of either acid or alkali employed in the titration ; moreover, another acid HR, having a smaller degree of ionisation than HM, will indicate the transition with even greater precision, providing that the recognition of the colour-change is not more difficult. The quantity of indicator employed must be so small that the amount of alkali required to neutralise it is negligible.

For Theory of Indicators, *v.* Ostwald (Scientific Foundations of Analytical Chemistry, translated by McGowan), Küster (Zeitsch. anorg. Chem. 1897, 13, 127), Waddell (J. Phys. Chem. 1898, 2, 171), Vaillant (Compt. rend. 1903, 136, 1192), Stieglitz (J. Amer. Chem. Soc. 1903, 25, 1112; Amer. Chem. J. 1908, 39, 651 ; 1909, 42, 115), McKoy (Amer. Chem. J. 1904, 31, 503), Hewitt (Analyst, 1908, 33, 85), Salm (Zeitsch. physical. Chem. 1906, 57, 471 ; Zeitsch. Elek. Chem. 1907, 13, 125), Salessky (Zeitsch. Elek. Chem. 1904, 10, 204), Fels (Zeitsch. Elek. Chem. 1904, 10, 208), Schoorl (Chem. Zentr. 1907, i. 300, 502, 585), Hantzsch (Ber. 1907, 40, 1556 ; 1908, 41, 1187), Rohland (Ber. 1907, 40, 2172), Acree (Amer. Chem. J. 1908, 39, 528, 649, 789), Handa (Ber. 1909, 42, 3179); and *cf.* Noyes for the physico-chemical theory (J. Amer. Chem. Soc. 1910, 32, 815).

Indicators may be divided broadly into three classes : (i.) Those insensitive to very weak acids, such as carbonic, boric, and hydrosulphuric acids; these indicators comprise among others *methyl orange, lacmoid, cochineal,* and *iodoeosin.* (ii.) Those somewhat sensitive to weak acids, although as a rule these acids cannot be accurately titrated with their aid; if weak volatile acids such as carbonic acid are removed by boiling, these indicators act like those of the first class towards fairly strong acids and bases. *Litmus* is the chief representative of this group. (iii.) Those highly sensitive even to weak acids. This class contains *phenolphthaleïn, turmeric,* and *rosolic acid* (*v.* Glaser, Zeitsch. anal. Chem. 1899, 38, 273 ; Wagner, Zeitsch. anorg. Chem. 1901, 27, 138).

The more important indicators are described below in alphabetical order.

Aurin (*Commercial or para-Rosolic acid*) is a mixture of several substances, produced by heating together phenol and oxalic and sulphuric acids; it appears in commerce in yellowish-brown resinous lumps. A 1 p.c. solution in 60 p.c. alcohol is employed, 0·5 c.c. being added to the solution to be titrated. In acid solution the colour is pale *yellow,* in alkaline solution *rose-red.* This indicator is very sensitive and well adapted for titrating barium hydroxide solutions, but it is affected by carbon dioxide and hydrogen sulphide.

Cochineal. The colouring matter in the product obtained from the dried female insect *Coccus cacti* (Linn.), is termed *carminic acid.* The best trade product, which is called ' silver cochineal,' was first recommended as an indicator by Luckow (J. pr. Chem. 1861, 84, 424 ; Zeitsch. anal. Chem. 1862, 1, 386) ; 3 grams of the substance (not pulverised) is extracted with 250 c.c. of dilute alcohol (1 vol. alcohol : 3–4 vols. water), and the clear liquid decanted. In alkaline solution the colour is *violet,* in acid *yellowish-red.* This indicator, which is very sensitive to strong acids and bases, is extremely useful in titrating ammonia ; it is scarcely affected by carbon dioxide. The colour-change is well defined even in artificial light. Cochineal is, however, useless for titrating organic acids ; and iron, aluminium and copper salts must be absent, since their solutions remain pink even when acid.

Curcumin (*Turmeric yellow*). The colouring matter from the roots of *Curcuma longa* (Linn.), is turned *yellow* by acids and *reddish-brown* by alkalis ; it is nearly always employed as a *test-paper,* and is useful in detecting ammonia and boric acid.

Galleïn (*Alizarin violet, Pyrogallolphthaleïn*). This compound, prepared by heating together pyrogallol and phthalic anhydride (Baeyer, Ber. 1871, 4, 457, 555, 663), was proposed as an indicator by Dechan (Pharm. J. 15, 849). A 0·1 p.c. alcoholic solution is used, 10 drops being added to 100 c.c. of liquid. In alkaline solution the colour is *reddish-violet,* in acid *pale-brown.* This indicator is scarcely affected by carbon dioxide, and can be used in the accurate titration of organic acids.

Iodoeosin (*Tetraiodofluoresceïn, Erythrosin B.*). This substance, prepared by iodating fluorescein, is a brick-red powder soluble in hot alcohol or in ether, but almost insoluble in water or cold alcohol ; it was first recommended by Mylius and Förster (Ber. 1891, 24, 1482) ; 0·5 gram of the sodium derivative of iodocosin is dissolved in 1 litre of water, 2·5 c.c. are added to the solution to be titrated together with 5 c.c. of chloroform, the mixture being shaken in a stoppered bottle during titration. While alkaline the aqueous layer is *rose red,* when acid the aqueous layer becomes *colourless,* and the chloroform assumes a yellowish tint (Ellms, J. Amer. Chem. Soc. 1899, 21, 359 ; M. and F. used ether instead of chloroform). With this indicator, centinormal or even millinormal solutions can be titrated ; it is indifferent to carbon dioxide, and phosphoric acid can be titrated as a monobasic acid with sodium hydroxide (Glücksmann, Chem. Zentr. 1902, (i.) 1131). Feeble bases, such as the alkaloids, may also be titrated, using iodoeosin as indicator.

Lacmoid (*Resorcin Blue*). This substance is obtained by heating gradually to 110° a mixture of 100 parts of resorcinol, 5 parts of sodium nitrite, and 5 parts of water. When the violent reaction moderates, the mass is heated to 115°–120° until evolution of ammonia ceases. The product is a glistening reddish powder (Traub and Hock, Ber. 1884, 17, 2615).

A 0·3 p.c. alcoholic solution is employed ; a better colour change is produced if 5 grams of naphthol green are dissolved in a litre of this solution (Zeitsch. angew. Chem. 1890, 3, 163). In alkaline solution the colour is *blue* ; in acid, *red.* Although these colour changes resemble

those of litmus, the indicator is more closely allied to methyl orange. It is only slightly affected by carbon dioxide, although direct titration of carbonates is not satisfactory in cold solution; lacmoid test paper may, however, be used in almost any experiment for which methyl orange is suitable. This indicator is useless for organic acids.

Litmus occurs in commerce in the form of small cubical granules mixed with a large proportion of calcium carbonate. An aqueous solution of this product not only contains free alkali, but also a variable proportion of colouring matters which interfere with the delicacy of the reaction. Special precautions must therefore be taken in preparing the solution for use in acidimetry. Various processes have been recommended by Berthelot and De Fleurieu (Ann. Chim. Phys. 1865, [4] 5, 189), Wartha (Ber. 1876, 9, 217), Mohr (Titrirmethode), Luttke (Zeitsch. anal. Chem. 1892, 31, 692). The following method gives excellent results : The litmus is extracted three or four times with boiling methylated alcohol of 85 p.c. in order to remove the injurious colouring matters, the residue is extracted with cold water, slightly acidified with sulphuric acid, and boiled to expel carbon dioxide. The extract is neutralised with baryta water, a few bubbles of carbon dioxide passed in to remove excess of baryta, and the liquid again boiled and filtered. The solution should contain about 20 grams of solid matter per litre, and must be kept in vessels to which the air has free access. If kept in closed vessels it undergoes fermentation and is decolourised. The colour is restored when the liquid is exposed to air. The colour of the solution should be *purple*; it turns *blue* with alkalis, and *red* with acids, and is affected by carbon dioxide, sulphur dioxide, and hydrogen sulphide. (For the relative merits of litmus and methyl orange, *v.* Reinitzer, Zeitsch. angew. Chem. 1894, 547, 574; Lunge, *ibid.* 1894, 733.)

The colour change is rendered more delicate by conducting the titration in the monochromatic light obtained by heating a bead of sodium carbonate in a bunsen flame (L. Henry, Compt. rend. 1873, 76, 222). The red solution seems colourless, whilst the blue solution is almost black. Litmus is not well adapted for use by gas- or lamp-light.

Luteol. The preparation of this substance, a hydroxychlorodiphenylquinoxaline, is described by Autenrieth (Arch. Pharm. 1895, 233, 43), and by Glaess and Bernard (Mon. Sci. 1900, 14, 809); it forms fine, woolly, yellowish needles, m.p. 246°. A 0·33 p.c. alcoholic solution is used as an indicator. In alkaline solution the colour is *yellow*; in acid it is *colourless*. This indicator is said to be remarkably sensitive, excelling Nessler's solution as a test for ammonia; but it is sensitive to carbon dioxide (Higgins, J. Soc. Chem. Ind. 1900, 19, 958). It was especially recommended by Autenrieth for use in Kjehldahl's process (*v.* ANALYSIS).

Methyl orange (*Helianthin, Poirrier's Orange III.*). This substance, prepared by diazotising sulphanilic acid and coupling the resulting diazonium salt with dimethylaniline, was introduced as an indicator by Lunge (Ber. 1878, 11, 1944; J. Soc. Chem. Ind. 1882, 1, 16). One gram of pure methyl orange (either the free acid or its

sodium salt) is dissolved in 1 litre of water, and two drops of this solution are added in each titration; if, owing to dilution during the titration, the colour becomes too faint, another drop of the indicator is added; on no account should too much indicator be used, since the colour change, from *yellow* in alkaline to *pink* in acid solution, is not sharp in such circumstances. Methyl orange is exceedingly useful, since its indications are practically unaffected by the presence of carbonic, hydrosulphuric, boric, and silicic acids; carbonates and sulphides may therefore be titrated in cold solution as if they were hydroxides. All titrations must be made with this indicator in cold aqueous solution, and, since methyl orange is not very sensitive as compared with various other indicators, the acid or alkali employed should be fairly concentrated. It is advisable to employ normal solutions, though with N/2 or even N/5 solutions it is possible to determine an end-point to within a single drop. With N/10 solutions, especially when carbonates are being titrated, there is a distinct *brownish* transition tint between the yellow and pink, and results may be uncertain to the extent of one or two drops (*cf.* Küster, Zeitsch. anorg. Chem. 1897, 13, 140).

The addition of indigo-carmine to methyl orange has been recommended by Luther (Chem. Zeit. 1907, 31, 1172), who states that the colour change is very pronounced. Ethyl orange is stated by Wieland to be even better than methyl orange (Ber. 1883, 16, 1989).

Methyl red. This substance, prepared by diazotising anthranilic acid and coupling the resulting diazonium salt with dimethylaniline, was introduced as an indicator by Rupp and Loose (Ber. 1908, 41, 3905). A 0·2 p.c. alcoholic solution is employed, and two drops of this are added in each titration. The colour change is from a pure *yellow* in alkaline to a *reddish-violet* in acid solution, and is very pronounced. This indicator is very sensitive, and can be used for titrating weak bases in centinormal solution. The precise extent to which it is affected by carbon dioxide has not yet been determined; but ordinary sodium hydroxide solutions containing a little carbonate can be accurately titrated in the cold.

Phenacetolin, first recommended by Degener (Zeit. d. Ver. f. d. Rübenzucker Industrie, 1881, 357; J. Soc. Chem. Ind. 1882, 1, 85), is prepared by boiling together for several hours molecular proportions of phenol, acetic anhydride, and sulphuric acid. The product is extracted with water to remove excess of acid, dried and dissolved in alcohol in the proportion of 1 gram to 500 c.c. It is *pale yellow* with alkalis, *red* with carbonates of the alkalis and alkaline earths, *colourless* or *pale yellow* with acids. It is used for estimating both hydroxide and carbonate when present in the same solution.

Phenolphthaleïn, obtained by heating phenol with phthalic anhydride and concentrated sulphuric acid (Baeyer, Annalen, 1880, 202, 69), was proposed as an indicator by Luck (Zeitsch. anal. Chem. 1877, 16, 322). One or two drops of a 0·5 p.c. alcoholic solution are used in each titration. In alkaline solution the colour is *red*; the acid solution is *colourless*. Owing to its very weak acid character, phenolphthaleïn is the indicator *par excellence* for organic acids; it

is useless, however, in the presence of ammonium salts, and since even carbonic and hydrosulphuric acids discharge the red colour, it is necessary to work with solutions free from these acids or titrate in boiling solution; hence its use is somewhat restricted. A convenient method of titrating organic acids with ordinary sodium hydroxide solutions using phenolphthaleïn as indicator, is described by Philip (Chem. Soc. Trans. 1905, 87, 991); *cf.* McCoy (Amer. Chem. J. 1904, 31, 503); and Schmatolla (Ber. 1902, 35, 3905).

Turmeric *v.* CURCUMIN.

Many other indicators have been proposed from time to time, among others the following :—

Alizarin (Schaal, Ber. 1873, 6, 1180); *Alizarin-red* 1. W.S. (Knowles, J. Soc. Dyers, 1907, 23, 120); *Congo-red*; *cyanine* (Schönbein, J. pr. Chem. 1865, 95, 449); *cyanogen iodide* (Kastle and Clark, Amer. Chem. J. 1903, 30, 87); *diaminazoatoluenesulphonic acid* (Troeger and Hille, J. pr. Chem. 1903, 68, 297); *ferric salicylate* (Weiske, J. pr. Chem. 1875, 12, 157; Wolff,

Compt. rend. 1900, 130, 1128; Gerock, Chem. Zentr. 1900, ii. 1294); *flavescin* (Lux, Zeitsch. anal. Chem. 1880, 19, 457); *fluorescein* (Krüger, Ber. 1876, 9, 1572; Zellner, Chem. Zeit. Rep. 1901, 25, 40); *hæmatoxylin* (Wildenstein, Zeitsch. anal. Chem. 1863, 2, 9); *metanil yellow* (Linder, J. Soc. Chem. Ind. 1908, 27, 485); *methyl-3-aminoquinoline* (Stark, Ber. 1907, 40, 3434); *extract of mimosa flowers* (Robin, Compt. rend. 1904, 138, 1046); *para-nitrophenol* (Langbeck, Chem. News, 1881, 43, 161; Spiegel, Ber. 1900, 33, 2640; Zeitsch. angew. Chem. 1904, 17, 715; Goldberg and Naumann, Zeitsch. angew. Chem. 1903, 16, 644); *paranitrobenzeneazo-α-naphthol* (Hewitt, Analyst, 1908, 33, 85); and *Poirrier's blue* C4B (Engel, Compt. rend. 1886, 102, 214).

The relative sensitiveness of the more important indicators and their behaviour under various conditions have been investigated by Wieland (Ber. 1883, 16, 1989), and especially by Thomson (Chem. News, 1883, 47, 123, 135, 184; 1884, 49, 32, 38, 119; 1885, 52, 18, 29), whose results are summarised in the following table :—

	Litmus	Lacmoid	Aurin	Methyl orange	Phenacetolin	Phenolphthaleïn
Sensitiveness . .	0·05	0·01	0·01	0·05	0·01	0·01
Hot solutions . .	Available	Available	—	—	—	—
Ammonia . . .	Available	Available	Available	Available	Available .	Not available
Ammonium salts .	Not affected	Not affected	Less sensitive	Less sensitive	Not affected	Not available
Neutral alkaline salt	Not affected	Not affected	Not affected	Less sensitive	Not affected	Not affected
Carbon dioxide .	Indefinite	Indefinite	Indefinite	Not affected	Colour changed	Indefinite
Hydrogen sulphide	Indefinite	Decolourised	Indefinite	Not affected	Not affected	Indefinite
Alkaline carbonates .	Indefinite	Indefinite	Indefinite	Alkaline .	Red colour	Alkaline
Alkaline bicarbonates	Indefinite	Indefinite	Indefinite	Alkaline .	—	Neutral
Sulphites . .	Indefinite	Alkaline.	Neutral .	Alkaline .	Not available	Neutral
Acid sulphites .	Indefinite	Neutral .	Acid .	Neutral .	Not available	Acid
Silicic acid . .	Neutral	Neutral .	Neutral .	Neutral .	Neutral .	Not available
Alumina . . .	Indefinite	Alkaline.	Indefinite	Alkaline .	Neutral .	Neutral
Boric acid. . .	Indefinite	Indefinite	Indefinite	Neutral .	Indefinite .	Indefinite
Sodium thiosulphate	Neutral	Neutral .	Neutral .	Neutral .	Neutral .	Neutral
Sulphides . . .	Alkaline	Not available		Alkaline .	Alkaline .	Alkaline
Hydrosulphides .	Indefinite	Not available		Alkaline .	—	Neutral
Potassium nitrite.	Neutral	—	Neutral .	Destroyed	Neutral .	Neutral
Oxalic acid . .	Available	Not available	Available	Not available	Not available	Available
Phosphoric acid .	Indefinite	Monobasic .	Indefinite	Monobasic	Indefinite .	Dibasic
Arsenic acid . .	Indefinite	Monobasic .	Indefinite	Monobasic	Monobasic	Dibasic
Arsenious acid .	Neutral	Neutral .	Indefinite	Neutral .	Neutral .	Indefinite
Phenol. . . .	Neutral	Neutral .	Neutral .	Neutral .	Neutral .	Indefinite

The sensitiveness is measured in c.c. of decinormal acid required to produce a distinct change when the volume of the liquid is 100 c.c. It should be borne in mind, however, that the sensitiveness of many indicators changes (usually diminishes) in the presence of considerable quantities of dissolved salts. Where a reaction is given as ' indefinite,' it is not meant that there is no effect, but that the change is not sufficiently sharp to be available in analysis. In many cases where the reaction is indefinite in cold solutions it becomes definite if the liquid is boiled, *e.g.* litmus with sulphides, sulphites, and carbonates; phenolphthaleïn with sulphides and carbonates. Lacmoid *is* most serviceable in the form of paper, and several of the reactions which are unsatisfactory with the solution are sharp and distinct with the paper, *e.g.* with carbonates, sulphides, and sulphites.

Gawalowski recommends (Zeitsch. anal. Chem. 1883, 22, 397) the use of a mixture of methyl orange and phenolphthaleïn, which is deep-red with excess of alkali, pale-yellow when neutral, and rose-red with excess of acid. Compare also Schlotz (Zeitsch. Elek. Chem. 1904, 10, 549) on mixed indicators.

Preparation of Standard Acids and Alkalis.

Standard solutions of acids and alkalis are usually prepared on the *normal* basis, the *normal* solution of a chemical reagent containing one gram-equivalent of the substance in one litre of the solution (*v.* ANALYSIS, Volumetric section).

In acidimetry and alkalimetry it is essential to have a standard solution of some acid or alkali, the concentration of which is known with great accuracy; this solution serves to standardise the others. Various suggestions have been made, but the general choice, at least for technical purposes, has fallen on hydrochloric acid as the standard acid; sulphuric acid is frequently employed and, less often, oxalic acid.

The commonest method of fixing the exact concentration of the hydrochloric (or sulphuric) acid consists in titrating the acid against weighed amounts of pure anhydrous sodium carbonate, a process originally employed by Gay-Lussac, and strongly recommended by Lunge, Sutton, and Treadwell. Separate weighed quantities of the pure carbonate are dissolved in 50–100 c.c. of cold distilled water, and each titrated with the acid, using methyl orange as indicator. The

concentration of the acid solution is calculated from each result, and the mean of the concordant values adopted as correct. Chemically pure sodium carbonate is obtainable in commerce, and should be free from all but traces of chloride and sulphate; it is dried in a platinum crucible with continual stirring for 20–30 minutes at such a temperature that the crucible bottom is barely red hot, or the crucible, embedded in sand, may be heated at 300° for half an hour. Pure sodium carbonate may also be prepared by heating the bicarbonate at a temperature not exceeding 300° (Lunge, Zeitsch. angew. Chem. 1897, 10, 522). Sulphates and chlorides are removed from the bicarbonate by washing with cold water. (For the preparation of pure sodium bicarbonate, v. Reinitzer (Zeitsch. angew. Chem. 1894, 7, 551), and North and Blakey (J. Soc. Chem. Ind. 1905, 24, 396).)

The foregoing method, although extensively used, has been adversely criticised, the chief objection being that it is impossible to dehydrate the carbonate or bicarbonate without losing a little too much carbon dioxide. It is asserted that sodium oxide is present even when the temperature of drying has not exceeded 170°; v. Kissing (Zeitsch. angew. Chem. 1890, 3, 262); Higgins (J. Soc. Chem. Ind. 1900, 19, 958); Sörensen and Andersen (Zeitsch. anal. Chem. 1905, 44, 156); North and Blakey (J. Soc. Chem. Ind. 1905, 24, 396); Sebelin (Chem. Zeit. 1905, 29, 638); but cf. Seyda (Chem. Zentr. 1899, (i.) 1164); Lunge (Zeitsch. anal. Chem. 1904, 17, 231; 1905, 18, 1520).

A satisfactory method of checking the values obtained by the carbonate method depends on the fact that sodium oxalate, when heated, is converted into sodium carbonate. As this oxalate can be prepared in a high degree of purity, the residue of carbonate theoretically obtainable from a known weight of oxalate can be calculated, and the presence of any sodium oxide is immaterial providing that all calculations are based on the original weight of sodium oxalate.

The weighed oxalate is carefully heated in a platinum crucible until all the separated carbon has been burnt off and the residual carbonate begins to fuse; the cooled residue is dissolved in water and titrated as already described; v. Sörensen (Zeitsch. anal. Chem. 1897, 36, 639; 1903, 42, 333, 512; 1905, 44, 156), Lunge (Zeitsch. angew. Chem. 1905, 18, 1520); and ANALYSIS, (Volumetric section, standardisation of permanganate).

From time to time many other standards have been proposed, and among others the following:—

Potassium tetroxalate; succinic acid (Phelps and Hubbard, Zeitsch. anorg. Chem. 1907, 53, 361; Phelps and Weed, *ibid.* 1908, 59, 114, 120); *borax* (Rimbach, Ber. 1893, 26, 171); *potassium hydrogen tartrate* (Borntrager, Zeitsch. anal. Chem. 1892, 31, 43); *potassium dichromate* (Richter, Zeitsch. anal. Chem. 1882, 21, 205); *potassium iodate* (Fessel, Zeitsch. anal. Chem. 1899, 38, 449); *potassium biiodate* (Meineke, Chem. Zeit. 1895, 19, 2); *sodium* (Hartley, Chem. Soc. Trans. 1873, 26, 123; Neitzel, Zeitsch. anal. Chem. 1893, 32, 422; cf. Hopkins, J. Amer. Chem. Soc. 1901, 23, 727); and *sulphuric acid*, prepared by electrolysing copper

sulphate solution (Hart and Croasdale, Chem. News, 1891, 63, 93; Kohn, J. Soc. Chem. Ind. 1900, 19, 962).

Hydrochloric acid. In preparing a normal solution advantage may be taken of the fact that an aqueous solution of hydrogen chloride which boils at a constant temperature has a practically constant composition. A quantity of ordinary concentrated acid is distilled from a capacious retort until one-third has passed over. The residual liquid will contain 20·2 p.c. of hydrogen chloride, and 165 c.c. when diluted to 1 litre will form an almost exactly normal solution; it should be standardised by one of the following processes.

The strong acid is diluted until its specific gravity is approximately 1·1, and distilled; after three-fourths of liquid have passed over, the remaining distillate is collected apart, and the barometric height observed. The final quarter of the distillate is of perfectly definite composition, and the following table gives the actual content of hydrogen chloride for a definite barometric height, together with the weight of distillate which contains one gram-equivalent of hydrogen chloride, *i.e.* which yields a normal solution when diluted to 1 litre:—

Barometer	%HCl	Grams of mixture containing 1 mol. HCl
770	20·218	180·390
760	20·242	180·170
750	20·266	179·960
740	20·290	179·745
730	20·314	179·530

These results were calculated from the observed weights of liquid, without reduction to vacuum standard; the compositions were determined gravimetrically by precipitation as silver chloride (Hulett and Bonner, J. Amer. Chem. Soc. 1909, 31, 390).

The simplest method of preparing a large quantity of nearly normal hydrochloric acid is to find the approximate composition of the ordinary concentrated acid by taking its specific gravity with a hydrometer and referring to a suitable table; the requisite quantity of the acid is then measured out and appropriately diluted with distilled water.

To standardise the solution, it is titrated against successive weighed quantities of pure sodium carbonate (or sodium oxalate), as described above. Each separate amount of carbonate should weigh from 2·0 to 2·5 grams, in order to ensure a burette reading of 40 to 50 c.c. It is best to use methyl orange for indicator, since the titrations can be rapidly and accurately carried out in the cold; if litmus is used, the titration must be made in boiling solution. In the latter case, it is quicker to add a measured excess of acid to the carbonate, and titrate back with sodium hydroxide the value of which is known in terms of the acid; but the titration must nevertheless be done in boiling solution. The calculation is very simple: if x grams of sodium carbonate require y c.c. of hydrochloric acid, then 1 c.c. acid = x/y grams of sodium carbonate. Now, 1 c.c. N.-acid = 0·05300 grams sodium carbonate, and hence

concentration of acid = $\dfrac{x}{0·053y}$ times normal

= z times normal, say. As a rule, this is a very

convenient method of expressing the result; *e.g.* if the acid is used to estimate an alkali of equivalent e, then 1 c.c. acid $= \dfrac{e}{1000} \times z$ grams of alkali. If necessary, the acid solution may be diluted with distilled water so that the ratio final volume $\div$ initial volume $= z$; it will then be exactly normal. A simple arithmetical calculation is required, and if this process is contemplated, care should be taken initially to ensure that z shall be slightly greater than unity.

Hydrochloric acid is most accurately standardised gravimetrically by precipitating chlorine with excess of silver nitrate and weighing the silver chloride in a Gooch crucible. The solution may be titrated against pure silver according to the Mint process for assaying this metal. The method may be modified by adding the silver solution in very slight excess, this excess being determined in the filtrate with N/10-thiocyanate (Thorpe's Quantitative Analysis; Dittmar's Quantitative Analysis; Knorr, J. Amer. Chem. Soc. 1897, 19, 814; Hopkins, *ibid.* 1901, 23, 727). These methods are trustworthy only when the hydrochloric acid is free from chlorides.

A simple and accurate process of standardisation consists in immersing weighed pieces of Iceland spar in a measured volume of the acid, and noting the loss in weight of the spar after the acid is neutralised (Masson, Chem. News, 1900, 81, 73; Green, *ibid.* 1903, 87, 5; *cf.* Thiele and Richter, Zeitsch. angew. Chem. 1900, 13, 486).

Small quantities of standard hydrochloric acid may be prepared by absorbing dry hydrogen chloride in a weighed quantity of water and ascertaining the increase in weight (Moody, Chem. Soc. Trans. 1898, 73, 658; Higgins, J. Soc. Chem. Ind. 1900, 19, 958; Acree and Brunel, Amer. Chem. J. 1906, 36, 117).

Sulphuric acid. An approximately normal solution is obtained by diluting to 1 litre 28 c.c. of pure concentrated sulphuric acid (sp.gr. 1·84).

The solution may be standardised with pure sodium carbonate or oxalate (*v.* HYDROCHLORIC ACID), or a measured quantity treated with a slight excess of ammonia, evaporated to dryness, and the residual ammonium sulphate heated at 120° and weighed. This method gives trustworthy results only when pure redistilled acid is employed in preparing the solution (Weinig, Zeitsch. angew. Chem. 1892, 5, 204; Shiver, J. Amer. Chem. Soc. 1895, 17, 351; Hopkins, *ibid.* 1901, 23, 727; Marboutin and Pécoul, Bull. Soc. chim. 1897, 17, 880).

A measured volume of the acid is added to a weighed excess of sodium carbonate in a platinum dish, the solution evaporated, the residue dried at 300° and weighed. The change in weight due to the transformation of sodium carbonate into sulphate indicates the amount of acid present in the solution. This method is much preferable to precipitating and weighing the acid as barium sulphate (*cf.* Richardson, J. Soc. Chem. Ind. 1907, 26, 78).

Sulphuric acid solutions of definite concentration may be prepared by specific gravity measurements (Pickering, Chem. Soc. Trans. 1890, 57, 64). A quantity of the purest acid is diluted with half its volume of water, and the specific gravity of the mixture accurately determined at 15° or 18° in a Sprengel pyknometer. The percentage of sulphuric acid in the solution is then obtained by reference to tables giving the values for 15°/15° or 18°/18° (*v.* Sutton's Volumetric Analysis, 9th ed., or J. Soc. Chem. Ind. 1899, 18, 4). The table given in J. Soc. Chem. Ind. 1902, 21, 1511, may be employed when the specific gravity (15°/15°) has been calculated without introducing any vacuum corrections, which must be allowed for if the other tables are employed. Between the limits of 66 p.c. and 81 p.c. the following formulæ reproduce the values in the tables with an error not exceeding 0·04 p.c. :—

$$P = 86\, S_{15} - 69 \cdot 00$$
$$P = 86\, S_{18} - 68 \cdot 82$$

where P = percentage of sulphuric acid, and S_{15} and S_{18} = the specific gravities referred to water at 15° and 18° respectively, calculated without allowing for 'air displaced' (Marshall, J. Soc. Chem. Ind. 1899, 18, 4). The diluted acid may be kept in a stoppered bottle without change, and by weighing out the appropriate amount and diluting to a litre, a normal solution of sulphuric acid can be rapidly prepared.

Oxalic acid. A normal solution is prepared by dissolving 63·03 grams of the recrystallised hydrated acid $H_2C_2O_4 + 2H_2O$ in water and diluting to 1000 c.c. As the crystallised acid is somewhat efflorescent, especially on slightly warming, it may contain less than two molecular proportions of water. The solution may be checked against a standard alkali, using phenolphthaleïn as indicator, or against an accurately standardised permanganate solution (*cf.* Treadwell-Hall, Analytical Chemistry, vol. 2).

Oxalic acid solutions do not keep very well.

Sodium hydroxide. To prepare a normal solution, clear transparent lumps of the best white commercial caustic soda are selected, any opaque portions of their surface scraped off, and 50 grams of the substance weighed out for each litre of solution. The cooled solution is standardised against the standard hydrochloric acid, using methyl orange as indicator, and taking 50 c.c. for each titration.

For the preparation of sodium hydroxide solutions free from carbonate, *v.* Küster (Zeitsch. anorg. Chem. 1897, 13, 134; 1904, 41, 472, and Bousfield and Lowry, Phil. Trans. 1905, 204, 253).

Potassium hydroxide *cf.* SODIUM HYDROXIDE.

Barium hydroxide. An approximately N/10-solution is best prepared from the crystalline hydroxide $Ba(OH)_2, 6H_2O$. The powdered substance is shaken with distilled water, the solution allowed to settle, the clear liquid siphoned off and diluted with an equal volume of recently boiled-out water. The solution must be kept permanently in contact with that portion already in the burette, and guard tubes are required to prevent access of carbon dioxide. The solution is standardised against succinic acid, phenolphthaleïn being used as indicator; or a measured volume may be evaporated to dryness with a slight excess of pure sulphuric acid, the residual barium sulphate being gently heated and weighed.

The chief use of this solution is in titrating organic acids, using phenolphthaleïn as indicator. For this purpose carbon dioxide must be excluded, and barium hydroxide is consequently the most convenient alkali to employ.

Ammonia. This solution is not often employed ; an approximately semi-normal solution, readily obta'ned by diluting 28 c.c. of concentrated ammonia solution to 1 litre, is titrated against hydrochloric acid in the cold, using methyl orange as indicator ; phenolphthaleïn cannot be employed.

Schultze has determined the rates of expansion of normal solutions of acids and alkalis and other solutions employed in volumetric analysis (Zeitsch. anal. Chem. 1882, 21, 170). The following are the results for average temperatures :—

—	Oxalic acid	Hydro-chloric acid	Nitric acid
0°	10000	10000	10000
10°	10010	10010	10018
15°	10019	10019	10031
20°	10031	10030	10045
25°	10046	10043	10061

—	Sulphuric acid	Potassium hydroxide	Sodium hydroxide
0°	10000	10000	10000
10°	10017	10019	10021
15°	10029	10031	10034
20°	10044	10046	10048
25°	10060	10062	10065

TYPICAL ACIDIMETRIC AND ALKALIMETRIC ESTIMATIONS.

Determination of total alkali. A weighed quantity of the substance (10 grams) is dissolved in water, filtered if necessary, and diluted to 500 c.c. ; 50 c.c. are withdrawn, mixed with a measured excess (25 c.c.) of normal acid, boiled gently for ten minutes to expel carbon dioxide, and the excess of acid determined with standard alkali. The volume of standard acid *minus* the excess of acid gives the volume of acid required to neutralise the total alkali, *i.e.* the alkali present as hydroxide, carbonate, sulphide, sulphite, thiosulphate, aluminate, and silicate. If methyl orange is used as indicator, boiling is unnecessary, and the alkaline solution is titrated directly with standard acid. If direct titration with litmus as indicator is preferred, the solution must be continuously boiled during the titration.

Alkaline hydroxide in presence of carbonate. 100 c.c. of the above solution are heated, mixed with excess of barium chloride, allowed to cool, diluted to 250 c.c. and well shaken. When the precipitate has settled, 50 c.c. of the clear liquid are withdrawn and titrated with standard acid. The quantity of acid used × 25 gives the volume equivalent to the hydroxide in the weight of substance originally taken. The reaction which takes place is expressed by the equation

$$x\mathrm{M_2CO_3} + y\mathrm{MOH} + (x + \tfrac{y}{2})\mathrm{BaCl_2}$$

$$= x\mathrm{BaCO_3} + \tfrac{y}{2}\mathrm{BaH_2O_2} + (2x + y)\mathrm{MCl}.$$
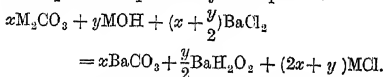
The barium carbonate is precipitated and a quantity of barium hydroxide equivalent to the

alkaline hydroxide remains in solution. The solution cannot be filtered, since the barium hydroxide would absorb carbon dioxide from the air with formation of the insoluble carbonate.

In order to avoid error due to the presence of the precipitate, and to economise time, Watson Smith (J. Soc. Chem. Ind. 1882, 1, 85) prefers to add just sufficient barium chloride to precipitate the carbonate without affecting the hydroxide. No barium remains in solution, and even if carbon dioxide is absorbed the alkaline carbonate formed remains in solution. The barium chloride is added gradually to the hot solution until precipitation is just complete, and the liquid is filtered into a 250 c.c. flask and an aliquot portion titrated. It is preferable for the liquid containing the precipitate to be diluted to 250 c.c., the precipitate allowed to settle, and 50 c.c. of the supernatant liquid withdrawn. (For various details and precautions, v. Sörensen and Andersen, Zeitsch. anal. Chem. 1908, 47, 279.)

Carbonate in presence of hydroxide. The solution is coloured a very faint yellow with phenacetolin, and standard acid is added until the yellow colour changes to a rose tint. The volume of acid required gives the amount of hydroxide present. A further quantity of acid is now added, and the red colour increases in intensity, but eventually changes to yellowish-red, and finally to golden-yellow. At this point a second reading is taken, and the difference between this and the first reading gives the volume of acid corresponding with the carbonate present (Lunge, J. Soc. Chem. Ind. 1882, 1, 56). This method is not available for the estimation of small quantities of hydroxide in presence of large quantities of carbonate (Thomson).

The following method, due to Warder, gives fairly satisfactory results : To the cold dilute solution phenolphthaleïn is added and standard hydrochloric acid run in slowly, the burette tip being immersed in the liquid, till decolourisation takes place. This occurs when all the hydroxide and *half* the carbonate have been neutralised. Methyl orange is then added and the solution titrated again till an acid reaction is indicated. If this second titration requires y c.c. and the first one x c.c., then the carbonate is equivalent to $2y$ c.c. and the hydroxide to $x - y$ c.c. (Küster, Zeitsch. anorg. Chem. 1896, 13, 127 ; Lunge, Zeitsch. angew. Chem. 1897, 10, 41 ; North and Lee, J. Soc. Chem. Ind. 1902, 21, 322 ; cf. Cameron, Amer. Chem. J. 1900, 23, 471).

In order to estimate the proportion of carbonate in quick-lime or slaked lime, the purpose for which phenacetolin was originally recommended by Degener, 100–150 grams of the lime are made into a cream with water and diluted to 500 c.c. After vigorous agitation 100 c.c. are withdrawn and diluted to 1000 c.c., and 25 c.c. of this liquid are taken, mixed with phenacetolin, and standard acid added until a pale-rose tint is obtained. In order to estimate both hydroxide and carbonate, the substance is dissolved in standard acid and the excess of acid determined by reverse titration in the usual way (Lunge, *l.c.*).

Acid carbonate in presence of normal carbonate. The *cold and dilute* solution of normal carbonate and acid carbonate is mixed with phenolphthaleïn, and standard acid added, the

burette tip dipping into the liquid to prevent escape of carbon dioxide, until the liquid becomes colourless. At this point, which corresponds with the complete conversion of the normal carbonate into acid carbonate, the volume of acid added is read off. The liquid is then boiled and acid is added gradually until the solution remains colourless even after long boiling, and the volume of acid is again read off. If x represents the first reading, and y the second reading, then $2x =$ the normal carbonate, and $y - 2x =$ the acid carbonate (Warder, Chem. News, 1881, 43, 228).

Lunge (J. Soc. Chem. Ind. 1882, 1, 57) proposes a different method based on the reaction:

$$xM_2CO_3 + yMHCO_3 + zNH_3 + (x+y)BaCl_2$$
$$= (2x+y)MCl + yNH_4Cl + (x+y)BaCO_3 + (z-y)NH_3.$$

The solution to be tested is mixed with a measured excess of standard (half-normal) ammonia, excess of barium chloride added, and the liquid diluted with recently boiled water to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn and titrated with standard acid in order to ascertain the excess of ammonia. The difference between the volume of ammonia added and that remaining after precipitation gives the volume corresponding with the quantity of acid carbonate in the liquid analysed.

By adding a definite excess of pure sodium hydroxide free from carbon dioxide, a mixture of normal carbonate and hydroxide is obtained which may be analysed as described above.

Ammonia. In order to determine the quantity of free ammonia in a solution of the gas, an accurately measured quantity (10 c.c.) of the liquid is transferred to a light tared flask, and weighed. This gives at once the weight taken for analysis and the sp.gr. The liquid is then titrated with standard acid in the usual way, using litmus, lacmoid, or methyl orange as indicator.

Ammonia in combination is determined by boiling the substance with sodium hydroxide, leading the ammonia into a measured excess of standard acid, and determining the residual acid with standard alkali. The substance is weighed into a flask fitted with a cork, through one hole in which passes a pipette containing a strong solution of sodium hydroxide, whilst through another passes a tube leading to a flask or bulb U-tube containing a known volume of standard acid. The flask or U-tube is fitted with a cork which carries a calcium chloride tube containing beads moistened with some of the acid in order to ensure complete absorption of the ammonia. After addition of the sodium hydroxide solution the liquid is gently boiled for half an hour, and the residual acid determined. From the volume of acid which has combined with the ammonia the quantity of the latter is readily calculated. The sodium hydroxide may be replaced by milk of lime, and the most effectual method of removing the ammonia is to distil the mixture in steam. The use of magnesia in place of sodium hydroxide is not advantageous (Kober, J. Amer. Chem. Soc. 1908, 30, 1279). (For a different method of distilling off the ammonia, v. Kober (J. Amer. Chem. Soc. 1908, 30, 1131). See also Ronchèse (J. Pharm. Chim. 1907, 25, 611) and Wilkie (J. Soc. Chem. Ind. 1910, 29, 6)

for a method of estimation entirely different in principle from the foregoing.)

Hydrochloric, Hydrobromic, Hydriodic, Sulphuric, and **Nitric acids** are readily estimated by direct titration with standard alkali, using methyl orange as indicator.

Oxalic, Tartaric, Citric, Acetic, and **Lactic acids** can likewise be titrated accurately with standard alkali if phenolphthaleïn is used as the indicator (Thomson, l.c.). Oxalic acid may also be titrated, using litmus as indicator.

Boric acid gives no very definite reaction with the majority of indicators, but it is quite neutral to methyl orange, and hence the quantity of alkali in alkaline borates can be accurately estimated by direct titration with standard acid if methyl orange is used as indicator (Thomson).

The titration of boric acid itself becomes possible if the solution contains at least 30 p.c. of its volume of glycerol. The boric acid then behaves towards phenolphthaleïn as a monobasic acid (Thomson, J. Soc. Chem. Ind. 1893, 12, 432; Jorgensen, Zeitsch. angew. Chem. 1897, 10, 5; Hönig and Spitz, ibid. 1896, 9, 549; Copaux, Compt. rend. 1898, 127, 756). A similar result is effected by saturating the solution with mannitol. Since phenolphthaleïn is employed, carbon dioxide must not be present in the solutions to be titrated (Jones, Amer. J. Sci. 1898, 7, 147; Stock, Compt. rend. 1900, 130, 516).

Sulphurous acid can be titrated directly if methyl orange, phenolphthaleïn, or aurin is used as indicator (Lunge, Dingl. poly. J. 250, 530). With methyl orange the hydrogen sulphite $MHSO_3$ is the neutral salt, whilst with the other two indicators the normal salt is neutral. This difference can be utilised for the determination of the relative proportions of normal and acid sulphite in the same solution (Blarez, Compt. rend. 1886, 103, 69; Chem. Soc. Abst. 1886, 50, 918). Caustic soda or potash must be used, since ammonia gives inaccurate results.

Phosphoric and **Arsenic acids** are monobasic with methyl orange, and dibasic with phenolphthaleïn (Joly, Compt. rend. 1882, 94, 529; Chem. Soc. Abst. 1882, 42,692). These acids can be most accurately titrated with barium hydroxide, using phenolphthaleïn as indicator. Towards the close of the reaction, time must be allowed for the gelatinous tribarium phosphate to change into the crystalline dibarium salt (Joly, Compt. rend. 1886, 102, 316; Chem. Soc. Abst. 1886, 50, 418). Advantage can be taken of the different basicity with methyl orange and phenolphthaleïn to estimate phosphoric acid in presence of monobasic acids such as hydrochloric acid (Joly, Compt. rend. 1885, 100, 55; Chem. Soc. Abst. 1885, 48, 348).

(For another simple and accurate method, v. Segalle, Zeitsch. anal. Chem. 1895, 34, 33.)

Carbonic acid in solution is estimated by adding excess of ammonia and calcium chloride. The liquid is then boiled, and the precipitated calcium carbonate collected, well washed, and dissolved in a measured excess of standard hydrochloric acid, the excess of acid being determined by means of standard alkali. The volume of normal acid actually used multiplied by 0·022 gives the quantity of carbon dioxide.

Insoluble carbonates are weighed into a flask fitted with a cork which carries a bulb and

delivery tube. The bulb contains moderately strong hydrochloric acid, which is allowed to drop slowly on the carbonate, and the evolved gas is led into a flask containing strong ammonia solution. This flask is closed with a cork, through which passes the delivery tube, which ends just above the surface of the liquid. The cork also carries an exit tube filled with glass beads moistened with ammonia to arrest the last traces of carbon dioxide. When all the gas has been expelled from the carbonate the ammonia is mixed with calcium chloride, boiled, and the precipitate treated as above; *cf.* Gooch and Phelps (Amer. J. Sci. 1895, 50, 101). With slight modification this process can be adapted to the estimation of carbon dioxide in aërated waters.

For the direct titration of carbon dioxide in solution, *v.* Seyler (Analyst, 1897, 22, 312); Ellms and Beneker (J. Amer. Chem. Soc. 1901, 23, 405); and Forbes and Pratt (J. Amer. Chem. Soc. 1903, 25, 742).

Hydrofluoric acid may be accurately titrated with sodium hydroxide free from carbonate, using phenolphthaleïn as indicator (Winkler, Zeitsch. angew. Chem. 1902, 15, 33; *cf.* Haga and Osaka, Chem. Soc. Trans. 1895, 67, 251; and J. Amer. Chem. Soc. 1896, 18, 415; Monatsh. 1897, 18, 749).

Hydrofluosilicic acid may be titrated with sodium or barium hydroxide in the presence of alcohol (an equal volume is added) using phenolphthaleïn or lacmoid as indicator; the alcohol renders the salt produced insoluble in the solution; *v.* Sahlbom and Hinrichsen (Ber. 1906, 39, 2609); *cf.* Schucht and Moller (Ber. 1906, 39, 3693); and Honig and Szabadka (Chem. Zeit. 1907, 31, 1207).

Combined acids in salts may be estimated with approximate accuracy by adding to a solution of the salt a measured excess of sodium hydroxide or carbonate. The liquid is boiled, allowed to cool, and diluted to a definite volume. When the precipitate has settled, an aliquot portion of the clear liquid is withdrawn, and the excess of alkali determined by titration. From the volume of alkali used the proportion of acid in the salt is calculated. In order to avoid the error due to the presence of the precipitate, the liquid may be filtered before diluting to a definite volume, but methyl orange or cochineal must be used as indicator in order to avoid any error from carbon dioxide absorbed from the atmosphere. Salts of copper, silver, mercury, cobalt, nickel, iron, and chromium are precipitated with sodium hydroxide; salts of calcium, barium, strontium, magnesium, aluminium, zinc, bismuth, and manganese, with sodium carbonate.

Kieffer's method is useful for coloured solutions, or in presence of normal salts with acid reactions (Annalen, 1855, 93, 386). Sixty grams of crystallised cupric sulphate are dissolved in water, mixed with ammonia until the precipitate is almost but not quite dissolved, diluted to about 900 c.c., the solution left for some time, and the clear liquid siphoned off, or filtered through glass-wool, and diluted to 1000 c.c. If any further precipitate forms, it must be siphoned off or collected. If the solution of cuprammonium sulphate thus obtained is added to an acid liquid, so long as the acid is in excess an ammonium salt and cupric sulphate are

formed, but as soon as the free acid is neutralised, the ammonia in a fresh quantity of cuprammonium sulphate reacts on the cupric sulphate already in the liquid and produces a precipitate of a basic salt, the formation of which indicates the point of saturation. The precipitate is most readily seen against a black background. In order to standardise the liquid, 10 c.c. of normal sulphuric acid are placed in a flask or beaker and Kieffer's solution added until a permanent precipitate is produced, and from the volume of solution required, its strength in terms of normal acid is readily calculated. The strength of the solution gradually diminishes, and it must be titrated from time to time. In making an actual determination, the Kieffer's solution is added to the liquid to be tested until a permanent precipitate is formed. The method is not very accurate, owing mainly to the fact that the precipitate is not quite insoluble in solutions of ammonium salts, and therefore the end reaction does not take place until the liquid is saturated with the basic salt. The magnitude of the error depends on the concentration of the solution. When the liquids to be titrated contain barium, strontium, &c., the Kieffer's solution must be prepared with cupric nitrate.

(For other methods, *v.* Sims (Chem. News, 1907, 95, 253) and Ahlum (Chem. Soc. Proc. 1906, 22, 63).)

Bibliography.—Mohr's Chemisch-Analytische Titrirmethode, 6th ed. 1886; Sutton's Volumetric Analysis, 9th ed. 1904; Fresenius' Quantitative Chemische Analyse, v. 2, 6th ed.; Treadwell-Hall, Analytical Chemistry, v. 2, 2nd ed. 1910; Lunge's Technical Chemist's Handbook; Cohn's Indicators and Test Papers, 2nd ed. 1902; Glaser's Indikatoren der Acidimetrie und Alkalimetrie, 1901.   G. T. M.

ACID ALIZARIN, -BLACK, -BROWNS, -PONCEAU, -YELLOWS *v.* Azo- COLOURING MATTERS.

ACID MAGENTA *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACID VIOLET *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ACIDINE BRILLIANT RED *v.* Azo- COLOURING MATTERS.

ACME YELLOW *v.* Azo- COLOURING MATTERS.

ACOKANTHERA SCHIMPERI. The arrow-poisons of East Africa are prepared from the wood of the genus *Acokanthera*, which contains a crystalline glucoside, *acokantherin* $C_{30}H_{46}O_{12}$, H_2O (Arnaud), $C_{32}H_{50}O_{12}$ (Faust). Crystallises from water and alcohol; insol. in ether or chloroform: sol. neutral and bitter. Strong sulphuric acid gives a red colour eventually becoming green. On boiling with dilute mineral acids is hydrolysed with formation of rhamnose. Is optically inactive, softens at 130° and decomposes at 220°. The pharmacological action of the glucoside resembles that of members of the digitalin group (Fraser and Tillie, Proc. Roy. Soc. 58, 70; Faust, Chem. Zentr. 1902, 2, [19] 1217).

ACONINE, ACONITE, ACONITINE, ACONITIC ACID *v.* VEGETO-ALKALOIDS.

ACORUS CALAMUS (Linn.). The common sweet flag. The root is used by distillers to flavour gin, and the essential oil by snuff-makers for scenting snuff. It contains a glucoside

termed *acorin* $C_{36}H_{60}O_6$ (Faust, Bull. Soc. chim. [2] 9, 392; Thoms, Arch. Pharm. [3] 24, 465) (*v.* CALAMUS).

ACRIDINE $C_{13}H_9N$. Crude anthracene contains basic substances, and among them acridine, which can be isolated by extracting it with dilute sulphuric acid and adding potassium dichromate to the acid solution. The precipitated acridine chromate is then recrystallised from water, treated with ammonia, and the base crystallised from hot water (Graebe and Caro, Annalen, 158, 265; Ber. 13, 99).

Acridine has also been obtained synthetically by passing the vapours of orthotolylaniline and of orthoditolylamine through a tube heated to dull redness (G., Ber. 17, 1370); by severally heating formic acid and diphenylamine (Bernthsen and Bender, Ber. 16, 767, 1802), chloroform, diphenylamine and zinc oxide (Fischer and Körner, Ber. 17, 101), and aniline and salicylaldehyde (Möhlau, Ber. 19, 2451) with zinc chloride; by passing *o*-amidodiphenyl methane through a layer of lead oxide heated to dull redness (Fischer and Schütte. Ber. 26, 3085). By distilling tetrahydroacridine with litharge (Borsche, Ber. 41, 2203), and also from acridone (Decker and Dunant, Ber. 39, 2720; Ullmann, Bader and Labhardt, Ber. 40, 4795).

Properties.—Acridine crystallises in small colourless needles, or four-sided rhombic prisms, sublimes at 100°, melts at 111°, boils above 360° without decomposition, and distils with steam. It is sparingly soluble in hot water, but readily soluble in alcohol, ether, or carbon disulphide, yielding solutions showing a blue fluorescence. When inhaled either as dust or vapour it causes violent sneezing, and in solution both it and its salts cause much irritation on the skin. On treatment with nitric acid it yields two nitroderivatives (m.p. 154° and 214°) and a dinitroderivative (G. and C.): potassium permanganate oxidises it to 2:3-quinolinedicarboxylic acid $C_9H_5N(CO_2H)_2$, and sodium amalgam reduces it to *hydroacridine* $C_{13}H_{11}N$ (B. and B., Ber. 16, 1971; G., Ber. 16, 2831). The salts are yellow and crystallise well, but are decomposed into their constituents on boiling. Heated with hydrogen and finely divided nickel, it forms 2:3-dimethyl quinoline (Padoa and Fabris, Atti R. Acad. Lincei, 1907, [v.] 16, i. 921). The halogen addition compounds of acridine and its derivatives are formed by the direct action of the halogen on the acridine (Senier and Austin, Chem. Soc. Trans. 1904, 1196); or by the action of a mixture of phosphorus oxychloride and pentachloride on thioacridone (Edinger, Ber. 33, 3770; D. R. P. 120586; Edinger and Arnold, J. pr. Chem. [ii.] 64, 132, 471; D. R. P. 122607); for other methods, compare Dunstan and Stubbs (Ber. 39, 2402; D. R. P. 126795), Graebe and Lagodzinski (Annalen, 276, 48). Alkyl iodomagnesium compounds of acridine have also been obtained (Senier, Austin, and Clarke, Chem. Soc. Trans. 1905, 1469). When exposed to sunlight acridine forms pale-yellow crystals, m.p. 276° (Orndorff and Cameron, Amer. Chem. J. 1895, 17, 658),.

2 : 7-dimethyl- 3 : 6-diaminoacridine or *acridine yellow* $NH_2 \cdot C_6H_2Me\underset{N}{\overset{CH}{\diagdown\diagup}}C_6H_2Me \cdot NH_2$ is obtained by heating under pressure tetraminoditolylmethane with hydrochloric acid and water,

the product is then oxidised with ferric chloride or potassium percarbonate $K_2C_2O_6$ or hydrogen peroxide, and the resulting metallic salt decomposed with hydrochloric acid (D. R. P. 52324; Lymn, J. Soc. Chem. Ind. 1897, 16, 406; Ullmann and Marić, Ber. 34, 4308; Haase, Ber. 36, 589). It forms yellow crystals melting above 300°, soluble in alcohol, acetone and pyridin, and forming a yellow solution in sulphuric acid with a green fluorescence. It yields derivatives which form yellow, orange, brownish-, greenish-, and reddish-yellow dyes, and can be used on cotton, leather, wool, and silk. The following are some of the methods of preparation: (1) heating with mineral acids under pressure, when it yields aminohydroxy- and dihydroxydimethyl acridine (D. R. P. 121686; Chem. Zentr. 1901, ii. 78; J. Soc. Chem. Ind. 21, 37); (2) heating with monochloracetic acid and water under pressure (D. R. P. 133788; Chem. Zentr. 1902, ii. 616; D. R. P. 136729; Chem. Zentr. 1902, ii. 1396); (3) heating with formaldehyde and mineral acids under pressure (D. R. P. 135771; Chem. Zentr. 1902, ii. 1233; J. Soc. Chem. Ind. 21, 112, 544, 402); (4) by treatment with formaldehyde and aromatic bases (J. Soc. Chem. Ind. 22, 140; D. R. PP. 131365, 132116; Chem. Zentr. 1902, ii. 172; i. 1288); (5) heating with benzyl chloride in presence of nitrobenzene (J. Soc. Chem. Ind. 21, 701, 1530); (6) treating with aqueous formic acid (*ibid.* 21, 90); (7) heating with glycerol at 150°–180° (D. R. P. 151206); (8) alkylation (Ullmann and Marić, *l.c.*; D. R. P. 79703; J. Soc. Chem. Ind. 19, 1010; 24, 840).

Phenylacridine $C_{19}H_{13}N$ is obtained by heating diphenylamine with benzoic acid and zinc chloride at 260° (Bernthsen, Ber. 15, 3012; 16, 767, 1810), and melts at 181°. The *hydroxyphenylacridines* which form yellow dyes in mineral acids can be obtained similarly by using the corresponding hydroxy acid (Landauer, Bull. Soc. chim. 31, 1083).

Other acridine dyes can be obtained by heating tetraminoditolylmethane or the leucocompounds of amino-acridines with mineral acid and alcohol under pressure, the shade depending on the quantity and nature of alcohol and of acid used (J. Soc. Chem. Ind. 20, 888; 22, 1126; 23, 932). Also by the interaction of an aromatic or aliphatic *m*-diamine with an aldehyde (*ibid.* 21, 1529; Chem. Zeit. 14, 334; J. Soc. Chem. Ind. 17, 573; 22, 1241). By heating the formyl derivatives of *m*-diamines with ammonia salts or salts of organic bases at 150°–200° (D. R. PP. 149409, 149410). For other methods of preparing acridine derivatives, many of which have dyeing properties, compare: Bizzarri, Gazz. chim. ital. 20, 407; Decker, J. pr. Chem. 153, 161; Mohlau and Fritzsche, Ber. 26, 1034; Volpi, Gazz. chim. ital. 21, ii. 228; J. Soc. Chem. Ind. 19, 732; 21, 338, 701, 911, 1528; Goodwin and Senier, Chem. Soc. Trans. 1902, 285; J. Soc. Chem. Ind. 22, 23, 90; D. R. PP. 133709, 107517; Ullmann, Ber. 36, 1017, 1025; D. R. P. 141297, 141356; Bünzley and Decker, Ber. 37, 575; Fox and Hewitt, Chem. Soc. Trans. 1904, 529; 1905, 1058; Schöpff, Ber. 26, 1121; Ber. 27, 2316; Duval, Compt. rend. 142, 341; Koenigs, Ber. 32, 3599; Ullmann and Maag, Ber. 40, 2515; Austin, Chem. Soc. Trans. 1908, 1760; D. R. PP. 118075,

152662; Pope and Howard, Chem. Soc. Trans. 97, 83.

Naphthacridine and its derivatives, which can also be used as dyes, have been prepared (J. Soc. Chem. Ind. 18, 826; 19, 237; Ullmann and Naef, Ber. 33, 905, 912, 2470; J. Soc. Chem. Ind. 20, 37, 573; D. R. P. 126444; Ullmann and Baezner, Ber. 35, 2670; 37, 3077; Ullmann and Felzvadjian, *ibid.* 36, 1027; Ullmann and Farre, *ibid.* 37, 2922; Ullmann and Fitzenham, *ibid.* 38, 3787; Baezner and Gardiol, *ibid.* 39, 2623; Baezner, *ibid.* 2650; Senier and Austin, Chem. Soc. Trans. 1907, 1233, 1240; Senier and Compton, *ibid.* 1907, 1927; Baezner and Gueorgnieff, Ber. 39, 2438).

In the case of many of the naphthacridine derivatives, patents have been taken by Ullmann (D. R. PP. 104667, 104748, 108273, 117472, 119573, 123260, 127586, 128754, 130721, 130943); the further alkylation of some of these, as well as of other acridine compounds has been patented by the A.-G. für Anilin-Fabrikation (D. R. PP. 117065, 129479).

ACRIDINE DYESTUFFS. Acridine, though colourless, shows absorption bands in the ultraviolet. The salts are yellow, and the addition products with alkyl halides are also coloured. (For absorption spectra, *see* Dobbie and Tinkler, Chem. Soc. Trans. 1905, 87, 269.) The salts of acridine itself are useless tinctorially, but amino- and alkyl-amino- derivatives of acridine, phenylacridine, &c., are useful dyestuffs, generally producing yellow shades. For the preparation of these substances, synthesis is generally resorted to, although acridine may be nitrated (Graebe and Caro, Annalen, 1871, 158, 275), and α-nitro-acridine has been reduced to an amino-acridine (Anschütz, Ber. 1884, 17,437).

One dyestuff of the acridine series, *chrysaniline*, is formed as a by-product in the manufacture of magenta (Hofmann, Jahresb. 1862, 346). Its constitution

$$C_6H_4 \underset{(1)C[(1)C_6H_4(4)NH_2](1)}{\overset{(2)N}{<}} C_6H_3(4)NH_2$$

was determined by O. Fischer and G. Körner; probably two molecules of aniline and one of *p*-toluidine condense when oxidised to *opp*-triaminotriphenylmethane, this yielding chrysaniline when further oxidised. This view is supported by the fact that when *opp*-triaminotriphenylmethane is heated with arsenic acid to 150°–180°, chrysaniline is produced (Annalen, 1884, 226, 188).

The processes for preparing amino- derivatives of acridine on a technical scale may be illustrated by the methods of preparing *benzoflavine, rheonine,* and *diaminoacridylbenzoic acid.*

Symmetrical diamino-acridines are obtained by the condensation of aldehydes with *m*-diamines, removal of the elements of ammonia from the resulting tetra-amino- compound by heating with hydrochloric acid, and oxidation of the dihydro-acridine thus produced with ferric chloride. In the case of *benzoflavine* benzaldehyde and *m*-toluylene-diamine are employed.

$$C_6H_5 \cdot CHO + 2 \overset{NH}{\underset{CH}{}} \overset{NH_2}{<} = H_2O +$$

The reaction is capable of considerable modification; thus from formaldehyde and dimethyl-*m*-phenylenediamine, *acridine orange* is produced in an analogous manner. It should be noted, however, that *m*-phenylenediamine gives products which are evidently mixtures, and cannot be purified (R. Meyer and R. Gross, Ber. 1899, 32, 2365).

The reaction between an aldehyde and a *m*-diamine may be carried out in two stages; Meyer and Gross (*l.c.* p. 2358), for example, prepared a monobenzylidene derivative of *m*-toluylenediamine and converted this into tetraminoditolyl-phenylmethane by warming its alcoholic solution with the hydrochloride of *m*-toluylenediamine for three hours at 60°–70°. Acridine itself may be obtained in good yield by heating salicylidene-aniline with phosphorus pentoxide to 250° (Blau, Monatsh. 1897, 18, 123).

A closely-related synthesis of acridine derivatives is that of F. Ullmann and E. Naef (Ber. 1900, 33, 905). When dihydroxydinaphthylmethane, the product of the interaction of formaldehyde and β-naphthol, is heated with *p*-toluidine hydrochloride, methylhydronaphthacridine is produced with elimination of β-naphthol.

$$CH_2(C_{10}H_6 \cdot OH)_2 + NH_2 \cdot C_6H_4 \cdot CH_3$$
$$= C_{10}H_7 \cdot OH + CH_2 \underset{C_6H_3(CH_3)}{} NH$$

Rheonine is obtained from *m*-aminophenyllauramine or tetramethyldiaminobenzophenone and *m*-phenylenediamine at 200°, using zinc chloride as condensing agent.

Some derivatives of xanthene, when energetically treated with ammonia, suffer replacement of the pyrone oxygen atom by an imino-group. By the prolonged heating of fluoresceïn with ammonia under pressure, R. Meyer (Ber. 1888, 21, 3376) obtained an acridine derivative, to which one of the three following constitutions is assignable :—

$$NH_2 \diagdown \diagup NH_2 \qquad N \diagdown \diagup NH_2$$

$$C_6H_4 \diagdown O \qquad C_6H_4 \diagdown \qquad \text{or}$$
$$CO \qquad\qquad COOH$$

$$NH \qquad NH_2$$
$$NH_2 \diagdown \diagup$$
$$C_6H_4 \diagdown CO \diagdown\diagdown\diagdown O$$
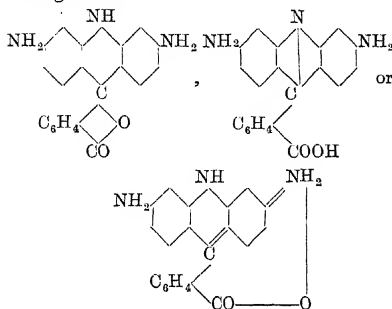
The salts of the tetra-ethyl derivative of this compound form the dyestuff known as *flaveosine*.

Acridine Orange NO (Farbwerk Mühlheim, D. R. P. 59179, 17 Dec. 1889), $C_{13}H_7N[N(CH_3)_2]_2$. HCl·ZnCl$_2$ was discovered by Bender. It is produced by condensation of dimethyl-*m*-phenylenediamine with formaldehyde and proceeding according to the method referred to above. It forms an orange powder which dissolves in water or alcohol with orange-red colour and greenish fluorescence. The aqueous solution is reddened by hydrochloric acid; sodium hydroxide gives a yellow precipitate. The solution in concentrated sulphuric acid is nearly colourless and has a greenish fluorescence, dilution with water produces successively red and orange colouration. The dye gives orange shades, fairly fast to light and soap, on cotton mordanted with tannin ; it is also suitable for printing and leather-dyeing.

The analogous dyestuff from diethyl-*m*-phenylenediamine is described in D. R. P. 67609, the substances derived from monoalkyl-phenylenediamines in D. R. P. 70935.

Another method of preparing acridine orange is to heat 12 kilos. of aminodimethylaniline either with 10 kilos. of formic acid (sp.gr. 1·2) and 10 kilos. of zinc chloride gradually to 150°–160°, or with 12 kilos. of dehydrated oxalic acid, 10 kilos. of glycerol and 11 kilos. of zinc chloride to 150°. Heating and stirring are continued as long as any darkening of shade can be observed, ammonia is liberated during the reaction, and formic acid having been employed instead of formaldehyde, the product when worked up yields the dyestuff instead of its leuco- compound (D. R. P. 67126).

The formyl derivatives of *m*-diamines may also be used (D. R. PP. 149049, 161699), or the 'methane' carbon atom may be furnished by various formyl derivatives such as formanilide (D. R. P. 149410).

Acridine Orange, R extra (Farbwerk Mühlheim, D. R. P. 68908, 7 Feb. 1890). The dyestuff is the hydrochloride of tetramethyldiamino-9-phenylacridine, and is obtained from dimethyl-*m*-phenylenediamine and benzaldehyde. Its reactions and uses are similar to those of Mark NO.

D. R. P. 68908 also mentions the use of *m*-aminodimethyl-o-toluidine. If the latter base be condensed with *p*-nitrobenzaldehyde to a triphenylmethane derivative, the nitro- group reduced and condensation and oxidation effected in the usual way, an acridine dyestuff possessing two tertiary and one primary amino- group is obtained (D. R. P. 70065; compare D. R. P. 71362).

The use of acetaldehyde as a component was claimed by the Ges. f. Chem. Ind. (D. R. P. 143893, 13 March, 1902).

Acridine Yellow (Farbwerk Mühlheim, D. R. P. 52324, 27 June, 1889) was, like the two preceding colours, discovered by Bender. Its constitution is that of a 3 : 6-diamino-2 : 7-dimethylacridine hydrochloride; it is produced from formaldehyde and *m*-toluylenediamine. It forms a yellow powder soluble in water and alcohol with yellow colour and green fluorescence; yellow precipitates are obtained with hydrochloric acid (hydrochloride) and sodium hydroxide (free base). Silk is dyed a greenish yellow with green fluorescence, cotton (tannin mordant) is coloured yellow.

The salts with aliphatic acids, *e.g.* formate and acetate, are more soluble (Farbenfabriken vorm. F. Bayer, D. R. P. 140848, 13 March, 1903). Acridine yellow is converted into an orange yellow, more easily soluble dyestuff by heating with twice its weight of glycerol for 4–6 hours to 170°–180° (Badische Anilin und Soda-Fabrik, D. R. P. 151206, 26 July, 1903).

(For the action of aldehyde on aniline yellow, *see* D. R. P. 144092.) Compounds, probably of acridinium type, are obtained from aniline yellow by the action of monochloracetic acid (M. L. B., D. R. PP. 133788, 136729, 152662) and other dyestuffs by condensation with formaldehyde and *m*-diamines (D. R. PP. 131365, 132116, 135771). Either one or both of the amino- groups in acridine yellow and analogous dyestuffs are replaced by hydroxyl on heating with dilute sulphuric acid to 180°–220° (D. R. P. 121686), and similar compounds may be obtained from formaldehyde by condensation with amino-cresols (D. R. P. 120466).

Dibenzyl aniline yellow is claimed by Bayer & Co. as a useful leather dye (D. R. P. 141297).

Benzoflavine (several marks), 3 : 6-diamino-2 : 7-dimethyl-9-phenylacridine hydrochloride $C_{13}H_4N(C_6H_5)(NH_2)_2(CH_3)_2$.HCl, was discovered by Rudolph in 1887, and introduced commercially by K. Oehler in 1888 (D. R. PP. 43714, 28 July, 1887 ; 43720, 45294, 45298). Its preparation has been given above. The dye, which is usually mixed with dextrin, forms an orange powder, difficultly soluble in cold water, more easily in hot. Both aqueous and alcoholic solutions are orange, with strong green fluorescence. Hydrochloric acid gives an orange precipitate, sodium hydroxide liberates the yellowish-white base. The solution in concentrated sulphuric acid is greenish yellow, and shows a very strong green fluorescence. It may be used for dyeing both mordanted and unmordanted cotton. The acetate and lactate are more readily soluble (Bayer, D. R. P. 142453, 19 April, 1902); it behaves like acridine yellow when heated with glycerol.

The **Patent Phosphines** of the Ges. f. Chem. Ind. in Basel are obtained by alkylation of benzoflavine and acridine yellow (D. R. P. 79703 ; compare D. R. P. 131289).

Coriophosphines (Bayer & Co.). These dye-stuffs, which are suitable for leather-dyeing, are probably unsymmetrically alkylated diamino-acridines obtained by condensation of formalde-hyde with one molecule of an asymmetrically dialkylated m-diamine and one molecule of a non-alkylated or monoalkylated m-diamine, with subsequent elimination of ammonia, and oxida-tion (D. R. P. 133709).

Chrysaniline $C_{19}H_{15}N$ occurs under many other names commercially, *e.g.* Leather yellow, Xanthine, Philadelphia yellow G, Leather brown, Phosphine (several marks), &c. Reference to its occurrence in the manufacture of magenta has already been made. Numerous methods for preparing homologues and analogues of this substance have been patented (D. R. PP. 65985, 78377, 79263, 79585, 79877, 81048, 94951, 102072, 106719, 114261, 116353). The method adopted for this purpose by Meister, Lucius, and Brüning may be mentioned (D. R. P. 65985, 2 April, 1892). *p*-Toluidine and its hydro-chloride are heated with ferric chloride (oxygen-carrier), and m-nitroaniline gradually added. The resulting dyestuff is the next higher homo-logue of chrysaniline, containing a methyl- group in position 7.

According to Friedländer (Fortschritte der Theerfarbenfabrikation V. 373), the yields pro-duced by this method are not good, but the reaction between p-aminobenzaldehyde and a derivative and phenyl-m-phenylene- (or toluyl-ene-) diamine proceeds nearly quantitatively :

$$C_6H_5 \cdot NH \cdot C_7H_6 \cdot NH_2 + C_6H_4(NH_2)CHO + O$$
$$= 2H_2O + C_6H_4 \overset{N}{\underset{C \cdot C_6H_4 \cdot NH_2}{<}} C_7H_5NH_2$$
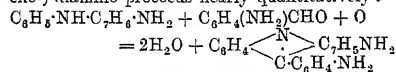
(B. A. S. F., D. R. PP. 94951, 102072).

Chrysaniline forms an orange-yellow powder, soluble in water and alcohol with reddish-yellow colour and yellowish-green fluorescence. The solu-tion is unaltered by hydrochloric acid ; sodium hydroxide gives a bright yellow precipitate. Chrysaniline is chiefly used in leather dyeing.

Corioflavines (Griesheim-Elektron). These dyestuffs, which occur commercially as marks G, GG, R, and RR, are used in leather-dyeing and calico-printing. They form red or reddish-brown powders, which dissolve in concentrated sulphuric acid with yellow or orange colouration and green fluorescence ; these solutions turn red or reddish-brown on dilution.

Flaveosine (Meister, Lucius, and Brüning, D. R. P. 49850, 11 May, 1889) is a tetraethyl-diaminoacridylbenzoic acid, which is obtained by heating m-acetaminodimethylaniline with phthalic anhydride. It has been examined by Grandmougin and Lang (Ber. 1909, 42, 4014).

The hydrochloride crystallises in shining brownish-yellow needles, the sulphate in prisms exhibiting a cantharides lustre. The base is precipitated from the salts by sodium carbonate, and forms golden-yellow shining leaflets.

Flaveosine dyes silk golden yellow (yellowish-green fluorescence) from a feebly acid bath ; wool and cotton (tannin mordant) are coloured reddish yellow. The colours are fast.

Substances closely related to flaveosine are obtained by the esterification of the product of the interaction of ammonia and fluorescein (B. A. S. F., D. R. PP. 73334, 75933 ; compare D. R. P. 141356).

Rheonine (Badische Anilin und Soda-Fabrik). This dyestuff was discovered by C. L. Müller (D. R. P. 82989, 16 Dec. 1894). Its method of preparation has already been given. Rheonine forms a brown powder, soluble in water and alcohol, with brownish-yellow colour and green fluorescence. Hydrochloric acid turns the solution brownish-red, caustic soda gives a bright brown precipitate. It is used for obtaining brownish-yellow shades on leather or cotton (tannin). Two marks, N (brighter) and A (darker), are in use.

The use of diaminobenzophenone and of Michler's hydrol for condensation with m-dia-mines have been patented (M. L. B., D. R. P. 89660 and B. A. S. F., D. R. P. 85199 re-spectively).

Many acridine and naphthacridine dyestuffs containing only one amino- group have been described (D. R. PP. 104667, 107517, 107626, 108273, 118075, 118076, 125697, 130360) ; and it has also been observed that dyestuffs can be obtained when only one molecular proportion of a m-diamine is used with formaldehyde (D. R. P. 136617). J. T. H.

ACRODEXTRINS *v.* DEXTRINS.

ACROSE *v.* CARBOHYDRATES.

ACTINIUM. A radioactive element, dis-covered by Debierne in the precipitate produced by adding ammonia and ammonium sulphide to the filtrate from the hydrogen sulphide precipi-tate obtained in the course of analysing pitch-blende (Debierne, Compt. rend. 129, 593 ; 130, 906). In fractionating the rare earths thus ob-tained from pitchblende by means of their double nitrates with magnesium nitrate, actinium accu-mulates in the more soluble portions together with neodymium and samarium (Compt. rend. 139, 538). The predominating rare earth in pitchblende is thorium ; but actinium also occurs in uranium minerals containing no thorium (Szilárd, Chem. Soc. Abstr. 1909, ii. 663).

Actinium has not been obtained pure, but it appears to resemble thorium chemically (*cf.* however, Giesel, Ber. 40, 3011). It is pre-cipitated by oxalic acid, hydrofluoric acid, and by ammonia. Actinium preparations are highly radioactive, imparting induced radioactivity to surrounding objects (Curie and Debierne, Compt. rend. 132, 548), and, like radium, they spontaneously give rise to helium (Debierne, Compt. rend. 141, 383) ; they are not lumines-cent. Their aqueous solutions slowly evolve hydrogen and oxygen in the proportions necessary to form water. Actinium salts also evolve an *emanation*, an inert gas having a molecular weight of approximately 70, according to diffusion experiments (Debierne, Compt. rend. 136, 446, 767 ; 138, 411 ; Bruhat, Comp. rend. 148, 628 ; Russ, Phil. Mag. 17, (vi.) 412), and condensing to a liquid at −120° to −150° (Kinoshita, Phil. Mag. 16, (vi.) 121).

The spontaneous decomposition of actinium appears to give rise to six successive products : *radio actinium* (Hahn, Ber. 39, 1605 ; Phil. Mag. 13, (vi) 165), which is said to resemble the

alkaline earths (Giesel, Ber. 40, 3011), and which changes into *actinium X*, a substance soluble in ammonia; this transforms into *actinium emanation*, from which *actinium A, actinium B,* and *actinium C* successively arise (Hahn and Meitner, Chem. Soc. Abstr. 1908, ii. 920); they are induced active deposits. Actinium itself is rayless; all the other products except actinium A emit α- particles; and radio actinium, actinium A, and actinium C emit β- rays (Hahn and Meitner, Chem. Soc. Abstr. 1908, ii. 1007).

Actinium is identical with the substance *emanium* discovered by Giesel (*v.* Giesel, Ber. 35, 3608; 36, 342; 37, 1696, 3963; Debierne, Comp. rend. 139, 538; Hahn and Sackur, Ber. 38, 1943; *cf.* Marckwald, Ber. 38, 2264).

ADAMANTINE SPAR *v.* CORUNDUM.

ADAMITE. An artificial abrasive made in Austria.

ADAMITE. Hydrated basic zinc arsenate, $Zn_3(AsO_4)_2 \cdot Zn(OH)_2$, crystallising in the ortho-rhombic system. First found in 1866 as violet crystals in a silver-mine at Chañarcillo, Chile, and subsequently as greenish and yellowish crystals in considerable abundance in the zinc-mines at Cape Garonne in France, and Laurion in Greece.

ADANSONIA DIGITATA (Linn.), the *Baobab tree*, yields a fibre which has been used in paper-making. Its bark (Gowik Chentz or Churee Chentz) is said by Duchaissaing to be a useful substitute for cinchona (Dymock, Pharm. J. [3] 7, 3).

ADENASE *v.* ENZYMES.

ADENINE, 6-*Aminopurine*

$$\begin{array}{c} N:C(NH_2)\cdot C\cdot NH \\ | \quad\quad || \quad\quad\quad\quad\rangle CH,3H_2O \\ CH:N\text{---}C\cdot N \end{array}$$
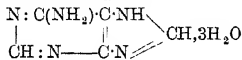
discovered in the pancreatic gland and spleen of the ox, occurs in all vegetable and animal tissues rich in cells (Kossel, Ber. 1885, 18, 79, 1928; Zeitsch. physiol. Chem. 1886, 10, 248); thus it has been extracted from tea leaves (Kossel, *l.c.*), from beet-juice (*v.* Lippmann, Ber. 1896, 29, 2645), from the young shoots of bamboo (Totani, Zeitsch. physiol. Chem. 1909, 62, 113); from human excretory products (Krüger and Schittenhelm, Zeitsch. Physiol. Chem. 1902, 35, 159), and from herring brine (Isaac, Chem. Zentr. 1904, ii. 647; from Beitr. chem. physiol. Path. 1904, 5, 500); it is probably one of the degradation products of nucleïn (Schindler, Zeitsch. physiol. Chem. 1889, 13, 432), and is found in small quantity when nucleïn is heated with dilute sulphuric acid (Kossel, Ber. 1885, 18, 1928).

Adenine is isolated from tea extract after the removal of caffeine by precipitating the cuprous compound $C_5H_3N_5Cu_2$ by means of copper sulphate and sodium bisulphite, and de-composing the precipitate with ammonium sulphide; the crude adenine is then isolated from the filtrate in the form of the sulphate. For the method of separating adenine from other purine bases compare Schindler, Zeitsch. physiol. Chem. 1889, 13, 432). The synthesis of adenine has been effected by reducing with hydriodic acid 2-amino-2 : 8-dichloropurine obtained by the action of aqueous ammonia on trichloropurine (E. Fischer, Ber. 1897, 30, 2226; 1898, 31, 104; Böhringer and Sons, D. R. P.

96927, 24/3, 97; Traube, Annalen, 1904, 331, 64).

Adenine crystallises from dilute aqueous solution in long rhombic needles that become anhydrous at 110°, and melt with decomposition when rapidly heated at 360°–365° (Fischer, *l.c.*), and sublime in microscopic needles without decomposition at 220°. Adenine is sparingly soluble in cold (1 : 1086) and readily soluble in hot water (1 : 40); insoluble in ether or chloro-form, sparingly so in alcohol. It forms com-pounds with bases, acids, and salts. The *nitrate* $C_5H_5N_5,HNO_3,\frac{1}{2}H_2O$ is crystalline, and the dry salt dissolves in 110·6 parts of water; the *hy-drochloride* $C_5H_5N_5,HCl,\frac{1}{2}H_2O$ forms transparent monoclinic prisms $a:b:c = 2\cdot0794 : 1 : 1\cdot8127$, $\beta = 61°\ 40'$ the anhydrous salt dissolves in 41·9 parts of water; the *chloracetate* $C_5H_5N_5$, $C_2H_3O_2Cl$ melts and decomposes at 162°–163°; the *sulphate* $(C_5H_5N_5)_2,H_2SO_4,2H_2O$, the *oxalate* $C_5H_5N_5,C_2H_2O_4,H_2O$, and *dichromate* $(C_5H_5N_5)_2$, $H_2Cr_2O_7$ are crystalline; the *picrate* $C_5H_5N_5$, $C_6H_3N_3O_7$ is stable at 220°, and is so sparingly soluble in cold water (1 : 3500) that it is used as a means of estimating adenine in solution (Ber. 1890, 23, 225); the *picrolonate* $C_5H_5N_5$, $C_{10}H_8O_5N_4$ crystallises from water and melts at 265° (Levene, Biochem. Zeitsch. 1907,4, 320). The *platinichloride* $(C_5H_5N_5)_2,H_2PtCl_6$ crystallises from dilute solution in needles, and yields the *salt* $C_5H_5N_5,HCl.PtCl_4$ when a concentrated solution is boiled. The *acetyl* derivative $C_5H_4N_5Ac$ does not melt at 260°, the *benzoyl* derivative $C_5H_4N_5Bz$ has m.p. 234°–235° (Kossel, Ber. 1886, 20, 3356). The *methyl* and *benzyl* derivatives have been prepared (Thoiss, Zeitsch. physiol. Chem. 13, 395). *Bromadenine* $C_5H_4N_5Br$ is strongly basic, forms an insoluble *picrate*, and on oxidation with hydrochloric acid and potassium chlorate yields alloxan, urea, and oxalic acid (Bruhns, Ber. 1890, 23, 225; Krüger, Zeitsch. physiol. Chem. 1892, 16, 329). Adenine is converted into hypoxanthine by the action of nitrous acid (Kossel, Ber. 1885, 18, 1928).

M. A. W.

ADHESIVES, as distinguished from cements, may be defined to be substances or preparations of a gummy or gelatinous character used for the purpose of joining together or effecting the mutual adhesion of the surfaces of bodies. They are usually substances which (1) soften in water, *e.g.* gum arabic, isinglass, glue, &c.; (2) gela-tinise in water or other menstruum, and harden either by the evaporation of the solvent or its absorption by the cohering surfaces, *e.g.* liquid glue, gelatine dissolved in acetic acid, rubber or guttapercha in benzene, &c.; or (3) which soften on heating and congeal on cooling, *e.g.* marine glue, shellac, &c. The surfaces of the articles to be joined should be perfectly clean; they should be brought into intimate contact, and as little of the adhesive as possible employed. In certain cases perfect contact is ensured by heating the parts to be joined to a temperature such that the adhesive solidifies only when union is effected.

Solutions of gum arabic, or of dextrin, or British gum, mixed with acetic acid, are fre-quently employed in the case of paper. Flour or starch mixed with water containing a little alum so as to form a thick cream, which is then heated to boiling, and when cold mixed

with oil of cloves, thymol, phenol, or salicylic acid so as to preserve it, makes an effective adhesive. A transparent paste may be made by the use of rice starch instead of ordinary flour. Occasionally a small quantity of linseed oil or glycerol is added in the case of labels exposed to moisture. Or the labels may be protected from damp by being coated with a mixture of 2 pts. shellac, 1 pt. borax dissolved in 16 pts. of boiling water. An alternative method is to apply a coating of copal varnish.

A strong adhesive may be made from shredded gelatine, swollen in water containing 25 p.c. of glacial acetic acid and applied hot. The mixture should be kept in a closely corked phial. Another recipe : Dissolve 60 pts. borax in 420 pts. water, add 480 pts. dextrin and 50 pts. glucose, and heat carefully—not above 90°—with constant stirring until the whole is in solution; replace the evaporated water and filter through flannel (Hiscox).

Wheat flour rich in proteins is mixed with concentrated sulphite liquors and evaporated to a suitable consistency (Robeson). Dry casein mixed with half its weight of borax and a sufficiency of water makes an excellent adhesive for broken china or earthenware. Milk casein dissolved in alkali and an alkaline silicate, such as water-glass, and mixed with a solution of magnesium or calcium chloride, also constitutes an effective adhesive.

Metallic surfaces after having been rubbed with an alcoholic solution of hydrochloric acid may be caused to adhere by means of a mixture of 10 pts. tragacanth mucilage, 10 pts. honey, and 1 pt. flour (Spon).

A *marine glue* may be made by dissolving 10 pts. caoutchouc in 120 pts. benzene, and adding the solution to 20 pts. melted asphaltum, the mixture being poured into moulds to consolidate. In order to use it the glue is soaked in boiling water and heated over a flame until liquid.

ADIPIC ACID. *Butane-α-δ-dicarboxylic acid* $CO_2H \cdot (CH_2)_4 \cdot CO_2H$. Obtained by the action of nitric acid on sebacic acid, or on tallow, suet, and other fatty bodies (Arppe, Z. 1865, 300 ; Laurent, Ann. Chim. Phys. [2] 66, 166 ; Bromeis, Annalen, 35, 105 ; Malaguti, Ber. 1879, 572). It is present in beet-juice (Lippmann, Ber. 1891, 3299), and may be obtained from Russian petroleum by distilling the fraction containing naphthalene hydrocarbons (Aschan, Ber. 1899, 1769). It may be prepared by the reduction of mucic acid (Crum-Brown, Annalen, 125, 19), saccharic acid (de la Motte, Ber. 1879, 1572), *iso*saccharic acid with hydriodic acid and phosphorus, or of muconic acid with sodium amalgam (Marquardt, Ber. 1869, 385); by heating β-iodopropionic acid with silver (Wislicenus, Annalen, 149, 221); by the electrolysis of the potassium salt of the monoethyl ester of succinic acid, whereby the diethyl ester of adipic acid is produced (Brown and Walker, Annalen, 261, 117) ; by oxidising cyclo-hexanone with potassium permanganate in the presence of sodium carbonate (Rosenlew, Ber. 1906, 2202; Mannich and Hancu, Ber. 1908, 575).

Adipic acid crystallises in monoclinic laminæ, melts at 149°, and sublimes at a still higher temperature (Wirz, Annalen, 104, 257). *Cyclo*pentanone is produced when the calcium salt is distilled, and no anhydride is obtained by the distillation of the acid. It is slightly soluble in water at the ordinary temperature, and has a great tendency to form supersaturated solutions (Dieterle and Hell, Ber. 17, 2221) ; readily soluble in hot alcohol and ether. It forms salts with most metals which are generally soluble in water and crystallisable. There are eight isomerides of adipic acid, all of which have been prepared.

ADIPOCERE (from *adeps*, fat ; and *cera*, wax). A peculiar waxy-looking substance, first observed by Fourcroy in 1786, when the *Cimetière des Innocents* at Paris was cleaned out. A large number of coffins had been piled together and had remained for many years ; the corpses in many of these were converted into a saponaceous white substance. Fourcroy placed this substance, together with cholesterol and spermaceti, in a separate class termed by him ' Adipocere.' Gregory (Annalen, 1847, 61, 362), observed a similar substance in the case of a hog which had died of an illness, and had been buried on the slope of a mountain-side. The substance was completely soluble in alcohol, contained no glycerides, and consisted, according to Gregory, of about 25 p.c. of stearic acid, and about 75 p.c. of palmitic and oleic acids (these three acids form the chief constituents of lard). The absence of lime was explained by Gregory as due to the solvent action of water saturated with carbonic acid, which continually ran over the carcase. Gregory fully recognised that the fatty acids had been formed by the hydrolysis of the fat, water having washed away all the glycerol simultaneously produced, and he clearly stated his view that from corpses of animals all nitrogenous and earthy constituents could be washed away, fatty acids only remaining behind. Ebert (Ber. 8, 775) in the main confirmed these results in the examination of a specimen of adipocere. On saponifying with potash, about 1 p.c. ammonia escaped and an insoluble residue (about 6 p.c.), consisting of lime, &c., from tissues, remained. A mixture of potassium salts was obtained, which by fractional precipitation with magnesium acetate yielded mainly palmitic acid. The last fraction, not precipitated by magnesium acetate, but by lead acetate, yielded a hydroxylated acid, the formula of which is given as $C_{17}H_{34}O_3$. This acid, termed by Ebert hydroxymargaric acid, melts at 80°, and is most likely 1 : 10 hydroxystearic acid of the melting-point 81°. The occurrence of this acid in the adipocere examined by Ebert is very likely, as he could not detect any oleic acid ; it would thus appear that in the course of time the oleic acid had been oxidised to 1 : 10 hydroxystearic acid. More recently Schmelck (Chem. Zeit. 1902, 11) found in the examination of three specimens of adipocere the following results :—

Melting-point	.	.	62·5°C.
Insoluble fatty acids	.		83–84 p.c.
Ash	.	.	1·7 p.c.
			(containing 83·5 p.c. CaO)
Unsaponifiable matter			16·7 p.c.
Acid value	.	.	197
Neutralisation value of the fatty acids		.	203
Iodine value	.	.	14

Tarugi (Gazz. chim. ital. 34, ii. 469) also states that adipocere consists chiefly of palmitic acid.

The formation of adipocere from animal matter had been studied in glass vessels filled with water by Kratter. Kratter's opinion that adipocere originates from the albuminoids must, however, be rejected as erroneous, for there can be no doubt that the free fatty acids are formed by the hydrolysis of the body fat. All the decomposition products of the albuminoids and the glycerol would be washed away, and the fatty acids would naturally form with the lime of the bones, lime soap, which may or may not be further hydrolysed by water, to free acid and lime, according to the conditions obtaining in the decomposition of the body. There can be little doubt that the hydrolysing action of the water is greatly assisted by the presence of enzymes which act as accelerators in the hydrolytic action of the water on the body fat.

J. L.

ADONIN *v.* GLUCOSIDES.

ADONITOL *v.* CARBOHYDRATES.

ADRENALINE. *Epinephrine, Suprarenine* $C_6H_3(OH)_2 \cdot CH(OH) \cdot CH_2 \cdot NH \cdot CH_3$. It may be obtained by extracting finely divided suprarenal glands with trichloracetic acid, concentrating the extract under reduced pressure and precipitating the adrenaline by the addition of ammonia (Abel, Ber. 1903, 1839; 1904, 368). Takamine (Chem. Soc. Abstr. 1903, i. 376, D. R. P. 131496) obtains a concentrated aqueous solution of the glands, renders it alkaline and precipitates the adrenaline by the addition of an ammonium salt or by passing carbon dioxide through the solution. The crude product is recrystallised from hot water. The constitution of adrenaline has been investigated by Jowett (Chem. Soc. Trans. 1904, 192), Bertrand (Compt. rend. 1904, 139, 502), Abderhalden and Bergell (Ber. 1904, 2022), and Böttcher (Ber. 1909, 253). Adrenaline has been synthesised from catechol. Catechol is treated with chloracetylchloride, and the resulting chloracetylcatechol condensed with methylamine, whereby monomethylaminoacetyl catechol is produced. Reduction of this with aluminium in the presence of mercuric sulphate yields adrenaline (Stolz, Ber. 1904, 37, 4149; Farb. Meister, Lucius and Brüning, D. R. PP. 152814, 155632, 157300; Chem. Zentr. 1904, ii. 270, 1487; 1905, i. 315. Other syntheses, *v.* Barger and Jowett, Chem. Soc. Trans. 1905, 967; Farb. Meister, Lucius and Brüning, D. R. P. 212206, Chem. Zentr. 1909, ii. 486; Böttcher. Ber. 1909, 42, 253; *cf.* Paulz, Ber. 1909, 42, 484). An aqueous solution rapidly oxidizes, becoming pink and finally brown (Takamine, Amer. J. Pharm. 1901, 73, 523). Fusion with potash converts adrenaline into catechol; potassium permanganate oxidises it to formic acid, oxalic acid, and methylamine (Jowett, *l.c.*).

Adrenaline is a very strong hæmostatic agent and an intravenous injection produces an enormous rise in blood pressure. The following reactions serve for its detection : (i.) a few drops of 1 : 1000 solution added to a solution containing copper sulphate and potassium cyanide give a characteristic red colour (Knill, Pharm. Zeit. 1907, 25, 115); (ii.) a characteristic odour resembling phosphoretted hydrogen is obtained by adding

VOL. I.—*T.*

a few drops of adrenaline solution to a little sodium hydroxide (Gunn and Harrison, Pharm. J. 1907, 78, 718); (iii.) a fine red colour is obtained by boiling a solution containing a little potassium iodate and a few drops of phosphoric acid with a few c.c. of the adrenaline solution. Adrenaline may be estimated colorimetrically by means of iodine and sodium thiosulphate (Abelous, Soulié, and Toujan, Bull. Soc. chim. 1905, 23, 624).

ADSORPTION *v.* COLLOIDS.

ADUROL. Trade name for a haloid substitution product of hydroquinone, used as a photographic developer.

AËRATED or MINERAL WATERS. Originally the term ' mineral water ' was used to describe natural spring waters containing small quantities of various salts in solution, and frequently saturated with carbon dioxide, hydrogen sulphide, or other gases. When these waters were first imitated by the artificial introduction of carbon dioxide into dilute saline liquids, they were known as ' aërated waters,' to distinguish them from the natural products. At the present time the two terms are employed indiscriminately, and as a rule the whole of the products of the manufacturer of aërated waters are popularly known as ' mineral waters.'

Natural Mineral Waters. In every quarter of the globe natural spring waters containing salts with medicinal properties are common, though fashion has made some more celebrated than others. Some of these waters (*e.g.* Hunyadi Janos) contain magnesium and sodium sulphate, and have an aperient action, whilst others containing iron (*e.g.* Tunbridge Wells water) are valued as tonics. Others, again, like the waters of Harrogate, contain sodium sulphide (0·02 p.c.), and are used as remedies in various complaints.

The most widely consumed natural mineral waters are those which contain only a small proportion of salts and a large amount of carbon dioxide. Typical examples of these are Apollinaris water, Selters water, and St. Gaulmier (French).

The table of analyses (p. 50) show the chief constituents of typical natural mineral waters.

Small quantities of many other compounds are also present in all these waters, but the figures given above represent their main constituents. The composition of all natural mineral waters varies from time to time, but they preserve their general characteristics.

Artificial Mineral Waters. Special mixtures of salts approximately corresponding in composition to those in many of the well-known medicinal waters are now sold, with directions for preparing solutions, which, when aërated, shall produce passable imitations of the natural products.

Among the purely artificial mineral waters mention must be made of *seltzer water*, which is prepared somewhat upon the lines of the natural Selters water, and contains sodium carbonate, chloride, and sulphate, and sometimes calcium and magnesium chlorides, the proportion of these ingredients being varied to suit the popular taste of the district. It is bottled at a pressure of about 120 lbs., corresponding to about 45–55 lbs. in the bottle.

Other medicinal artificial mineral waters include soda-water, potash-water, lithia-water,

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PRINCIPAL SALINE CONSTITUENTS OF MINERAL WATERS—PARTS PER 10,000.

Source	Sodium carbonate	Sodium chloride	lum ate		m	Ma s			Calcium carbonate	m oxid and lumina	Carbon dioxide per litr	Authority
Apollinaris	12·57	4·66	3·00	trace			4·42		0·59	0·20		Bischoff and Mohr
Hunyadi Janos	7·96	13·05	159·15		0·85			160·16	9·33	0·04		Knapp
Kissingen	0·04	74·21	2·28	0·32			2·10		7·74	0·24	1026 at 11°C.	Kastner, Bauer, and Struve
Selters	8·01	22·51			0·47	0·51	2·60		2·43		1087 at 15°C.	Struve
Vichy	48·83	5·34	2·91	3·52			3·30		4·34	trace	508	Bouquet
Wiesbaden		68·35		1·46					4·18		200	Fresenius

and magnesia-water. Soda-water was an official drug in the London Pharmacopœia of 1836, but was not introduced into the British Pharmacopœia until 1867. In the present Pharmacopœia (1898) it is omitted, together with the other alkaline waters. There is thus now no standard for soda-water, and since the old standard of 30 grains of sodium bicarbonate to the pint is sometimes found too alkaline to be palatable, a large proportion of the soda water upon the market contains much less than the old specified proportion of alkali.

Methods of Aërating.—The process of impregnating water with carbon dioxide under pressure dates back to the middle of the 18th century, one of the earliest inventors of apparatus for the purpose being the Duke de Challons in France. In this country the artificial ' aëration' of water was suggested by Bewley in 1767, and in 1772 Priestley constructed an apparatus somewhat on the principle of the modern Kipps' gas generator. A similar apparatus was devised about the same time by Bergman, and was extensively used throughout Sweden.

The earliest processes of bottling aërated waters made use of what is known as the ' Geneva' or *semi-continuous* process, in which the carbon dioxide, after being generated from chalk and acid, was forced under pressure with water into a cylinder, whence it could be drawn off into the bottles. This process, which is still employed in modified forms, is useful when a relatively small amount of liquid is to be impregnated, but has the drawbacks of requiring the work to be interrupted to recharge the cylinder, and of bottling the liquid at lower pressures than are often required. Hence in most mineral-water factories the *continuous process* is employed. Although numerous patents in connection with aërating machinery have been taken out, the type of machine which originated with Bramah is still the one in general use.

In Bramah's continuous process the gas is generated in a leaden or lead-lined generator from sulphuric acid and a carbonate, and passes into a gasometer consisting of an inverted copper bell in a tank of water. Thence, after expanding, 'it is pumped, simultaneously with water, into a condenser or globe, where the water is finely divided and saturated with the gas under a pressure indicated upon a gauge. From this it passes into the bottling part of the machine, where each bottle, placed by hand in position, receives a measured quantity of concentrated sodium carbonate solution or of sweetened syrup and is filled up with the water charged with the gas.

A ' blow-off' valve is provided so that the air may be completely expelled from the bottle, and in some types of machines there are means for returning the excess of gas to the gasometer, though this is not altogether advantageous.

Arrangement of Apparatus.—The general mode of arranging the aërating apparatus in the factory is shown in the accompanying figure (p. 51). The generator, T, is now frequently replaced by cylinders of liquefied carbon dioxide, which are connected with the gasometer. The soda-water machine, properly so called, has one or two pumps for forcing the gas and the water into the condenser, O, the latter being made of gun-metal with a lining of pure tin, and capable of withstanding a pressure three or four times in excess of any normally employed. In small installations a gas-engine usually takes the place of a steam-engine.

Carbon Dioxide Supply.—The general use of liquefied carbon dioxide instead of that generated from acid and calcium carbonate is the chief improvement on the original method of bottling. The new method is less expensive, more convenient, and obviates the difficulty attending the older process of disposing of the residue of calcium sulphate from the generator.

Liquefied carbon dioxide collected from the fermenting tuns in breweries is sometimes employed, but in the writer's experience gas from this source not infrequently contains traces of volatile impurities, which impart an unpleasant flavour to soda-water.

Pressures for Aërating.—Soda-water and similar unsweetened mineral waters are usually bottled at a pressure of 100–120 lbs. to the square inch in bottles, and of 150 lbs. in siphons, whilst for lemonade and the like a pressure of 60–80 lbs. is employed. In the case of goods intended for export a much lower pressure (usually 40–50 lbs.) is generally considered sufficient. The figures here given are those indicated upon the pressure gauge of the machine, the
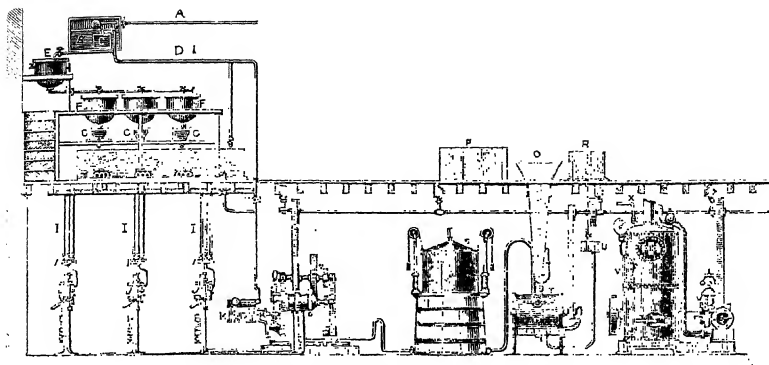
PLAN OF A SODA-WATER MANUFACTORY.

A. Main water supply from well or waterworks.
B. Water reserve.
C. Filter.
D. Pipe and branches supplying filtered water to syrup boiler, solution tank, and soda-water machine.
E. Steam-cased pan for boiling syrups.
FFF. Mixing and cooling pans for syrups.
GGG. Felt filtering bags, through which syrup is passed.
HHH. Tank in compartments for storing filtered syrups.
III. Syrup junctions and pipes supplying syrup pumps at bottling machines.
JJJ. Bottling machines.
K. Solution pan feeding soda-water machine with either plain water from filter C, or soda or other solution from tank L.

L. Soda-water solution tank for mixing mineral waters which require no syrup. When using this tank the tap M is closed.
M. Tap to shut off plain filtered water when bottling mineral water solutions.
N. Soda-water feed line.
O. Condenser containing aërated water, to which pipes leading to bottling machines are attached.
P. Whiting bin.
Q. Whiting shoot to generator.
R. Vitriol cistern.
S. Gasometer.
T. Generator.
U. Blow-back prevention acid box.
V. Steam engine.
X. Steam pipe to syrup boiler and bottle-washing apparatus.

actual pressure in the closed bottle being very much less. Thus experiments made by the writer have shown that the pressure within bottles of soda water bottled at a machine pressure of 100–120 lbs. does not exceed 45–55 lbs. An excess of pressure above a certain limit does not result in the liquid containing more gas.

An essential of good bottling is that all air should be expelled from the bottle, since otherwise, air being only slightly soluble as compared with carbon dioxide, the liquid will rush with almost explosive violence from the bottle, when opened, but will become flat almost immediately. On the other hand, a liquid properly saturated with carbon dioxide and free from air will continue to emit minute bubbles of gas for at least five minutes after it leaves the bottle.

Pressure Gauges.—The mode of measuring the pressure of the gas varies in different countries. Thus in England and the United States the zero mark on the dial of the pressure gauge indicates atmospheric pressure, and the succeeding figures represent the number of lbs. in *excess* of that pressure. In Germany the dial is graduated in atmospheric pressures in excess of the normal pressure, which is represented by zero; whereas in France, which adopts the same mode of expression, the figure 1 represents the normal pressure, and the figure 2 corresponds to 1 on the German scale and to 15 lbs. on the British and American scales, and so on.

Sweetened Aërated Drinks.—Lemonade, ginger ale, and similar sweetened 'mineral waters' are prepared in the same way as soda water. A thick syrup is made from sugar and saccharin and water, and this is acidified with citric or tartaric acid and flavoured with an essential oil, which is conveniently added in the form of an alcoholic solution termed a 'soluble essence.'

The syrups are filtered through the filter bags shown at C, C, C, in the diagram, into their respective tanks, H, H, H, whence they are drawn off into the bottling machine. The use of saccharin to replace part of the sugar in the syrups is almost universal in this country. It has the advantages of reducing the cost and of acting as a preservative, whilst its disadvantages are its cloying taste, which prevents its being used in more than a certain proportion, and the want of fulness on the palate of syrups containing it. The latter drawback is sometimes remedied by the addition of glucose syrup.

Methods of detecting and identifying saccharin are described by Boucher and Boungne, Bull. Soc. Chim. Belg. 1903, 17, 126 ; Analyst, 1903, 28, 241 ; von Maler, Farmaz. J. 1904, 1089 ; Analyst, 1904, 29, 374 ; Villiers, Ann. Chim. Anal. 1904, 9, 418 ; Analyst, 1905, 30, 21 ; Chace, J. Amer. Chem. Soc. 1904, 26, 1627 ; Jorgensen, Analyst, 1909, 34, 156.

Addition of Saponin.—The popular demand for a liquid which shall retain a frothy head for some time after it has left the bottle has led to the manufacturers frequently adding an extract of quillaia bark or other preparation of saponin, sold under the name of 'foam heading,' &c. Such an addition is more necessary in liquids containing saccharin than in all-sugar beverages, which froth more with the carbon

dioxide. According to the results of experiments made by Lohmann (Z. öffentl. Chem. 1903, 9, 320 ; Analyst, 1903, 28, 361), saponin has no injurious physiological effects. On the other hand, according to Bourcet and Chevalier (Pharm. J. 1905, 75, 691) commercial saponin contains neutral saponins of a toxic nature.

For the detection of saponin, see Brunner (Zeit. Untersuch. Nahr. Genussm. 1902, 5, 1197) and Rühle, *ibid.* 1908, 16, 165 (J. Chem. Soc. Ind. 1908, 27, 954).

Fermented Beverages.—The products of the mineral water factory include one or two beverages in which the aëration is the result of a limited fermentation.

Ginger beer, which is the type of this class, is prepared by adding sugar and citric acid to a dilute infusion of ginger root, infecting the liquid with a small quantity of a suitable yeast, bottling it, and allowing the bottles to stand at a proper temperature until sufficient fermentation has taken place.

As a rule the fermented liquid contains less than 1 p.c. of absolute alcohol, but occasionally in very hot weather the fermentation may proceed much further, and the ginger beer may then contain as much as 5 or 6 p.c. of alcohol. The pressure in the bottle of ginger beer when ready for consumption averages about 15 lbs. to the square inch, but in cases of abnormal fermentation it may reach 100 lbs. or more, and burst the bottle.

Occasionally objectionable flavours are produced by infection of the liquid with wild yeasts or bacteria, just as in the case of ordinary beer.

Other drinks of this description are horehound beer and other herb beers. Certain nonalcoholic ales on the market are prepared by partial fermentation of an infusion of malt and hops, which is then used as a syrup, and bottled with aërated water as in the case of lemonade.

Stoppers of Bottles.—The screw stopper of vulcanite or stoneware with a rubber ring to effect a tight joint is now universally employed ; for the glass ball-stopper (which had much to recommend it) has fallen into popular disfavour, and is now rarely met with, except in out-of-the-way districts.

The chief objection to the rubber-clad stopper is that impurities of various kinds may lodge beneath the rubber, and unless strict cleanliness is observed, may contaminate the contents of the next bottle into which it is introduced.

Bacteriological Conditions.—Until about two or three years ago it was commonly believed that sterilisation was effected by aërating a liquid with carbon dioxide under a high pressure. In 1908, however, bacterioscopic examinations were made, at the instigation of the medical officer for the City of London, of a large number of bottles of soda-water, and it was found that about 25 p.c. could be regarded as pure, and over 33 p.c. as impure, the remainder being ' fairly pure ' or ' not pure.' In some of the worst samples the numbers of micro-organisms per 1 c.c. at 20° were uncountable, and some yielded sediment from 50 c.c., which when cultivated at 37°, gave innumerable colónies.

As the result of this investigation a meeting of representative mineral water manufacturers

was held, and it was decided to adopt stringent measures to guard against bacterial contamination.

In addition to the obvious precautions of having a pure water supply and observing cleanliness in every stage of the manufacture, it was agreed to discard all wooden tanks and vessels (except for preliminary soaking to remove labels from old bottles), to rinse the bottles with water of assured purity immediately before filling, and to use for this purpose a metal jet of sufficient force. Wherever practicable, rubber rings were to be removed from the stoppers, or, failing that, were to be immersed in a solution of calcium bisulphite, and afterwards rinsed with pure water. The plant was also to be inspected by a competent authority.

There is no doubt that the adoption of such precautions has had the result of raising the standard of purity of soda-water throughout the country.

In considering the bacteriological aspect of the question, several points suggest themselves. Thus an unfavourable bacterioscopic examination of one or two samples taken casually does not necessarily imply faulty manufacture, for it may be the result of accidental contamination of the stopper by the hands of the worker—against which there is no complete safeguard.

Absolute sterility of the contents of the bottle should not be demanded, and it is unreasonable to require a greater degree of purity than that of the average water supply of London. Given a sufficient degree of purity of the original water, which is essential, efficient inspection of the factory at irregular intervals is a better protection than an occasional bacterioscopic examination. When such examinations are made periodically, they should be made under comparable conditions, *i.e.* at the same intervals after bottling ; otherwise the product of the cleaner process may show the worse results.

Standards are notoriously difficult to fix, but making allowance for the various chances of contamination, an average sample of soda water, examined one day after bottling, should not yield more than 100 organisms per 1 c.c. at 20°, or contain sufficient *B. coli* to be discoverable in 10 c.c.

Preservatives in Mineral Waters.—The preservatives most likely to be met with in unsweetened mineral waters are sulphites and bisulphites, solutions of which are frequently used, as in breweries, for cleansing the plant.

A small proportion of salicylic acid is often employed to prevent fermentation in the so-called ' fruit syrups ' and other sweetened articles, which might otherwise ferment and be the subject of an excise prosecution for containing alcohol.

Fermentations occurring in Mineral Waters.— Excessive fermentation of ginger beer is not uncommon in very hot weather, and the writer has met with samples containing as much as 6 p.c. of absolute alcohol.

Occasionally acetic or lactic fermentation may take place, and spoil a batch of goods, but this seldom happens when thorough cleanliness is observed.

A troublesome form of fermentation, commonly termed the ' mucoid fermentation,' results in the conversion of the contents of the bottle into

a thick ropy gelatinous mass. This may be caused by several micro-organisms, such as *B. gelatinosum betæ* or *B. viscosus sacchari*, and is more liable to occur when beet sugar is used for the syrup than when cane sugar is used. When it occurs in an isolated bottle, insufficient cleansing is a chief factor in its production.

Metallic Impurities.—Mineral waters not infrequently contain traces of metallic impurities, especially iron, tin, and lead, derived from the materials used or from some part of the plant.

Iron in soda-water is objectionable from the fact that, when the beverage is added to a light-coloured liquid, such as whiskey, containing a trace of tannin, an unpleasant dark colouration is produced.

Traces of tin find their way into mineral waters through the action of acid syrups upon the tin piping leading to the bottling machines, whilst lead may be derived from solder on the pipes. No such soldering should be permitted, and thorough flushing of tin piping with water night and morning effectually prevents contamination with tin. A still better safeguard, which has been adopted by some factories, is to replace the tin pipe by glass tubes with rubber connections.

A still more common source of lead is the citric or tartaric acid, in which it is frequently present as a manufacturing impurity.

Copper is not a common impurity, and, when present, is usually due to accidental contact of the acid syrup with the metal.

Arsenic may be derived from glucose used in the preparation of the syrups, or from the use of preparations of phosphoric acid instead of citric or tartaric acid for acidifying the syrups.

It has been asserted that mineral waters take up traces of antimony from the rubber rings of the stopper (which contain a large proportion of antimony sulphide). Experiments made by the writer, however, have shown that even a boiling 5 p.c. solution of hydrochloric acid does not dissolve any antimony from red rubber, and that there is thus no risk of mineral waters being contaminated in this way.

(For the detection of traces of metallic impurities in mineral waters, *see* Budden and Hardy (Detection of Lead, Tin, Copper, and Iron), Analyst, 1894, 19, 169 ; Tatlock and Thomson (Lead in Citric and Tartaric Acid), Analyst, 1908, 33, 173 ; Lander and Winter (Poisonous Metals), Analyst, 1908, 33, 450 ; Report of Conjoint Committee on Arsenic Determination, Analyst, 1902, 27, 48 ; Report of Royal Commission (Arsenic), Analyst, 1904, 29, 60 ; Thorpe (Electrolytic Determination of Arsenic), Analyst, 1908, 28, 349).   C. A. M.

ÆRUGO. (Verdigris (?) or basic carbonate of copper.) The name given by the Romans to the green rust produced on copper and bronze by the united action of the oxygen and carbon dioxide of the air. It was considered by them to enhance the beauty of their bronze statues. The same rust forms on brass, which was, however, not used by the Romans.

ÆSCULIN *v.* GLUCOSIDES.

AETHUSA CYNAPIUM (Linn.). ' Fool's parsley ' or the ' lesser hemlock,' a poisonous umbelliferous herb. When dried and extracted with alcohol, yields on distillation a small quantity of an essential oil, and the residue contains a resin, a crystalline hydrocarbon *pentatriacontane* $C_{35}H_{72}$ (m.p. 74°) and a crystalline alcohol (m.p. 140°–141° : $[a]_D = -35.7°$) either isomeric with phytosterol $C_{26}H_{44}O$, or a lower homologue ; *d-mannitol*, together with a small quantity of a *volatile alkaloid* resembling conine, to which the alleged poisonous character of the herb may be due (Power and Tutin, J. Soc. Chem. Ind. 1905, 938).

AFFINITY, CHEMICAL *v.* CHEMICAL AFFINITY.

AFRICAN ELEMI *v.* OLEO-RESINS.

AFRICAN GREEN or **EMERALD GREEN** *v.* PIGMENTS.

AFRICAN INCENSE *v.* OLEO-RESINS.

AGALITE. A name used in the paper-making trade for a fibrous variety of the mineral talc, a hydrated magnesium silicate, $H_2Mg_3Si_4O_{12}$. It is white with a tinge of green, and is readily reduced to short, fine fibres. It is obtained almost exclusively from the district near Gouverneur, in St. Lawrence Co., New York, about 70,000 tons, valued at $10 per ton, being produced annually. With the exception of a small quantity exported to Germany, it is all used in the American paper trade. It gives weight and body, and produces a fine gloss on the surface of the paper.   L. J. S.

AGALMATOLITE, or Pagodite. A soft stone much used in the East, especially in China, for carving small statues and figures, as signified by these names. At least three mineral species appear to be included under these terms, viz. pyrophyllite, steatite, and pinite ; but it is to the compact forms of the first of these that they are perhaps more generally applied. In addition to their compact nature and low degree of hardness, they have in common a greasy or soapy feel : in colour they are white, greyish, greenish, yellowish, &c., often with mottling. Pyrophyllite is a hydrated aluminium silicate, $H_2Al_2Si_4O_{12}$; steatite, a hydrated magnesium silicate, $H_2Mg_3Si_4O_{12}$; and pinite is an alteration-product consisting largely of a finely scaly muscovite-mica, a hydrated potassium aluminium silicate, $H_2KAl_3Si_3O_{12}$. Besides being employed as material for carving, these minerals are used for slate-pencils (' pencil-stone ') and for tailor's chalk (' French chalk ').

Extensive beds of compact pyrophyllite are quarried in the Deep River region in North Carolina, the material being mainly used for making slate-pencils. At Fukuye, in Goto Island, in the south of Japan, a compact mineral allied to pyrophyllite is mined under the name of ' rōseki ' (meaning ' greasy stone ' in Japanese) ; it is crushed, washed, and prepared very much like china-clay, and the product used for making fire-bricks, and to a smaller extent in the manufacture of porcelain and paper. This material contains SiO_2 53–58, Al_2O_3 32–36, H_2O 7–9 p.c.
     L. J. S.

AGAR-AGAR. Bengal Isinglass. Dried seaweed obtained from Singapore. It is obtained from various red algæ, including *Gelidium corneum, G. cartilagineum, Eucheuma spinosum,* and *Gracilaria lichenoides,* which grow along the coasts of Eastern Asia and Malaya. The cell-walls of these seaweeds, when placed in boiling water, change into jelly.

It occurs in small transparent strips or as

a powder, and dissolves almost entirely in water to a gelatinous, tasteless, and inodorous jelly. It is widely used as a nutritive medium for the cultivation of bacteria and fungi (*v.* ALGÆ).

AGAROBILLA. The seed-pods of *Cæsalpina brevifolia* (Baill.), used in dyeing and tanning.

AGATE. (*Achat,* Ger.) A natural aggregate of various forms of crystalline, crypto-crystalline, and colloidal silica. In most agates these siliceous minerals are arranged in alternating layers, which present on section a banded appearance, whence the agate is valued, when cut and polished, as an ornamental stone. This zoned structure is usually the result of the deposition of silica in successive layers within the cavities of a vesicular rock. In some cases, however, the deposition has been effected in fissures, thus forming siliceous veins, as in the brecciated agates of Saxony and Bohemia. In other cases the agates may occur in the cavities of stratified rocks, or occupy the spaces between the pebbles of a conglomerate : such are the agates of the dolomitic conglomerate and the ' potato stones ' of the Triassic marls of Somersetshire.

The artificial deposition of silica, in forms closely resembling those of certain agates, has been effected by I'Anson and Pankhurst (Min. Mag. v. 1882, p. 34). A strong acid is introduced by means of a pipette into a solution of an alkaline silicate, containing a certain proportion of alkaline carbonate ; the bubbles of carbon dioxide set free become coated as they ascend with gelatinous silica, which forms a tube ; and by continued deposition a stalactiform agate is produced. If a cavity in a rock were filled with a solution of an alkaline silicate, and the rock permeated by an acid, a layer of amorphous hydrated silica would be deposited upon the walls of the cavity, and through this gelatinous layer further deposition might gradually proceed.

The rocks in which agates typically occur are the basic igneous rocks known as basalt, dolerite, diabase, and melaphyre. These ' traps ' are essentially plagioclase-augite rocks. In many cases they present a vesicular texture, and the vesicles may enclose various secondary minerals resulting from the decomposition of the constituents of the rock. Among the commonest of these alteration-products is the green earthy mineral known as *delessite,* a hydrated silicate of aluminium, iron, and magnesium, probably a product of the decomposition of the augite. Many vesicles are simply lined with this green substance, but in other cases the delessite becomes covered by subsequent mineral deposits until the cavities are more or less completely filled. The rock thus becomes ' amygdaloidal;' a term suggested by the fact that the kernels of mineral are usually of almond-like shape. This shape is due to the cavities, which were originally gas- or steam-bubbles, having been elongated by the flow of the lava-like rock when viscous. In many cases the ' amygdules,' or contents of the cavities, are kernels of calcite, but in other cases they are siliceous. If hollow they form *geodes ;* and when nearly filled with alternate layers of chalcedony, jasper, quartz, and other forms of silica, they constitute true

The embedded agates are easily detached from the enclosing rock, and when removed

usually present a pitted surface. On the exterior is a green coating or ' skin ' of delessite, or of the similar mineral *chlorophæite :* many of the larger agates, however, present a rusty coating of ferric hydrate. The earliest-formed siliceous deposits are usually chalcedonic, and the latest are often crystalline : thus in a hollow agate the interior is generally lined with a crop of quartz crystals, not unfrequently amethystine, the apices of the pyramidal crystals being directed towards the central cavity. This structure shows that the agate has been formed by successive deposition from without inwards : in other words, the growth has been endogenous.' It is notable that in certain agates the first-formed layers have been concentric with the walls of the original cavity, and the subsequent strata horizontal.

Tubular orifices, lined with siliceous deposits, may be detected in many agates, and these have been commonly regarded as inlets of infiltration, or channels through which the siliceous solution gained access to the interior. It has, however, been held by many observers that the solution, so far from having been introduced through a definite aperture, gradually filtered in at all points ; and the internal walls thus became uniformly coated with a gelatinous layer, which allowed the further introduction of silica by osmotic action. Heddle pointed out that if, by a difference in the density of the siliceous solutions within and without the cavity, pressure were exerted outwards against the gelatinous medium, this deposit might give way, and the so-called inlet would thus be really a point of egress (Nature, 1884, p. 419). E. Reusch has suggested that the agate-bearing cavities were filled periodically with hot siliceous solutions by the action of intermittent thermal springs (Pogg. Ann. 1864, p. 94). G. Lange, extending this view, supposes that the steam from the solution confined in the cavity might exert sufficient pressure outwards to pierce the gelatinous deposit, and thus an outlet of escape might be mistaken for an inlet of infiltration.

Agates, when released from their matrix by its natural disintegration, occur as loose nodules, either in the beds of rivers or scattered over the country in pebble-drifts. The ' Scotch pebbles ' are found chiefly near Montrose in Forfarshire, and at the Hill of Kinnoul in Perthshire. The agates of the Cheviots are found in the Coquet and other Northumbrian rivers. In India agates have for ages been worked by the lapidaries of Cambay, Broach, and Ratanpur, who obtain their supply from the traps of the Deccan and of the Rájmahál Hills, or from the agate-bearing gravels of Rajpipla, which are systematically mined (Man. Geol. India, pt. III. [V. Ball], 1881, p. 503; pt. IV. [F. R. Mallet], 1887, p. 70).

The largest and finest agates are the so-called Brazilian stones, which come chiefly from the State of Rio Grande do Sul in Brazil, and from the neighbouring country of Uruguay. Here they are mostly found as pebbles in the beds of rivers, especially the R. Taquarie, having been derived from amygdaloidal trap rocks. Some interesting agates have been obtained from Uruguay, consisting of a rind of chalcedony, lined with quartz crystals, and containing liquid, movable within. These have been called *water-stones, hydrolites,* or

enhydros. According to C. W. Gümbel, the liquid is water with a small quantity of NaCl, $CaCl_2,CaSO_4,SiO_2,CO_2$, &c. (Sitz. B. z. München, 1880, II. p. 241 ; 1881, III. p. 321). Chalcedonic waterstones, of polyhedral form, occur at Beechworth, Victoria.

Moss-agate consists of chalcedony enclosing twisted filaments, usually green but sometimes red or brown, resembling vegetable structures. *Mocha-stones* are simply white or brown chalcedony, generally from India, with dendritic or arborescent markings due to oxides of iron and manganese. *Fortification-agate* is a term applied to those stones in which strata of jasper and chalcedony have been deposited upon quartz crystals, and hence they present on section curious zigzag patterns, suggestive of the plan of a fortress. The trivial terms *eye-agate, riband-agate,* &c., need no explanation.

Agate is employed for the knife-edges of balances, for small mortars and pestles, for burnishers and writing styles, for trinket-boxes, umbrella-handles, seals, brooches, beads, and an endless variety of trivial ornaments. Nearly all the agate used in the arts is worked in Germany.

The industry of cutting and polishing agates is centred in the neighbourhood of Oberstein on the river Nahe, a tributary to the Rhine at Bingen. Most of the agate-mills are situated near Idar, about two miles north of Oberstein. Here the Idar Bach, which flows into the Nahe, furnishes abundant water-power, which for four centuries has been utilised in the local mills. The original location of the trade in this district was due to the occurrence of agates in the amygdaloidal melaphyre of the Galgenberg, near Idar, where agates were formerly obtained by systematic mining operations. For many years, however, these workings have been abandoned, and the mills have been supplied with South American agates, the importation of which was begun about 1827.

Large consignments of South American agates are periodically sold by auction at Oberstein. The common stones are first roughly dressed with hammer and chisel, while the finer stones are carefully wrought into form by means of metal discs fed with emery or with diamond powder. The grinding is performed on wheels of red sandstone, about 5 feet in diameter, set vertically, and rotating at the rate of about three revolutions per second. Each stone is about 1 foot in width, and its surface presents channels corresponding with the form of the objects to be ground. The stones are usually moved by large undershot water-wheels, but the inconvenience of their stoppage during the drought of summer or the frost of winter has led to the partial introduction of steam-power. When working, the grinder lies almost horizontally upon a wooden stool, hollowed to the shape of his body, and having his arms free. The agate is pressed forcibly against the grindstone, fed with water from above, while the workman obtains purchase by pressing his feet against a block fastened to the floor. The polishing is afterwards effected with rouge and water on soft metal plates or with tripoli on wooden cylinders.

Not only agates, but rock-crystal, amethyst, false crocidolite, and other hard stones are now extensively cut and polished by the Idar lapidaries. These stones are also cut, to a limited extent, at Waldkirch in the Black Forest.

For many years the German agate-workers, following the earlier practice of the Italian cameo-cutters, have modified the colour of most of the stones by staining them. The commonest practice is that of darkening certain layers in a banded agate, so as to produce an *onyx.* The onyx presents a succession of two or more strata, alternately light and dark brown, or even white and black. To produce this contrast of colour when not naturally present, the agate is first steeped in honey and water, and gently heated on a stove. In course of time, perhaps two or three weeks, certain layers of chalcedony, more porous than others, are found to have absorbed the saccharine matter. No perceptible change is observed when the agate is removed and washed ; but on placing it for a short time in sulphuric acid the absorbed matter becomes carbonised, and it is then seen that certain layers of chalcedony, originally of a dull grey tint, have assumed a rich brown or even black colour. In place of the honey, olive oil is sometimes used. If accidentally coloured too strong, the excess may be removed, or the colour ' drawn,' by the use of nitric acid. The process of darkening agates is one of great antiquity, and is imperfectly described by Pliny (Hist. Nat. xxxvii. c. 75) as having been in his day practised in Arabia. On the history of colouring agates, *v.* Nöggerath, Die Kunst, Onyxe . . . zu färben, Karsten's Archiv. xxii. 1848, p. 262.

Carnelian is a red variety of chalcedony, and its characteristic tint may be easily developed artificially in the chalcedonic bands of certain agates which are, in their natural state, merely grey or yellowish. It has long been the practice in India to heighten the colour of pale brownish agates by prolonged exposure to solar heat, whereby any ferric hydrate in the stone loses more or less water. In Germany the agate is usually heated and then moistened with sulphuric acid, or is placed in a solution of ferric nitrate, prepared by throwing old nails into dilute aquafortis ; in either case the stone is afterwards exposed to a red heat, whereby the absorbed salt is decomposed and ferric oxide formed. Alternating bands of red and white chalcedony constitute the variety of agate known as *sardonyx,* and it is to imitate this stone that the red tints are often developed. Prolonged digestion in warm hydrochloric acid imparts a yellow tint to the agate, but this colour is not popular. Green colours, resembling those of *chrysoprase,* which is simply a green chalcedony, are produced by means of salts of either nickel or chromium. Blue tints may be readily obtained by soaking the stone in a solution of ferrous sulphate and afterwards in either ferrocyanide or ferricyanide of potassium, when Prussian blue or Turnbull's blue is formed in the pores of the stone ; or an ammoniacal solution of sulphate of copper may be used. Blue agates, artificially stained, are extensively sold as lapis-lazuli. More recently a dead-white effect has been produced in certain stones, which are thus rendered more valuable for cameo work. It is said that this effect is obtained by the use of caustic potash and subsequent exposure to a high temperature. On the agate industry, *v.* H. Lange, Die Halbedelsteine, Kreuznach, 1868 ;

hydrolysis the corresponding optically active alanines ; *r-alanine* decomposes at 264°–268° (Zelinsky and Stadnikoff, *l.c.*), at 293° (Fischer, Ber. 32, 2451) ; *d-alanine* has $[a]_D + 9.55°$ in hydrochloric acid solution ; *l-alanine* decomposes at 297° and has $[a]_D - 9.68°$ in hydrochloric acid solution. A cultivation of *Aspergillus niger* in an aqueous solution of *r-alanine* destroys about 10 p.c. of the dextrorotatory constituent, but *Penicillium glaucum* does not flourish in a 2 p.c. alanine solution.

In its physiological action, *d-alanine* causes a rapid rise in the urinary nitrogen, most of the extra nitrogen being excreted on the same day ; *l-alanine* is not decomposed quite so rapidly, but none of it is excreted unchanged (Abderhalden and Schittenhelm, Zeitsch. physiol. Chem. 1907, 51, 323 ; compare, however, Sevene and Meyer (Amer. J. Physiol. 1909, 25, 214). After administering 20 grms. of *r-alanine*, 4·7 grms. of the β-naphthalenesulphonic derivative of *l*-alanine was recovered from the urine (Schittenhelm and Katzenstein, Chem. Zentr. 1906, i. 1279). When *d-alanine* is injected in the blood-stream it is rapidly absorbed, as very little can be detected in the blood or urine after a lapse of twenty minutes (Abderhalden and others, Zeitsch. physiol. Chem. 1907, 53, 113, 251, 326 ; 52, 507 ; 53, 148).

The importance of alanine as a final hydrolytic product of many proteid substances, has led to an extensive examination of its derivatives in order to facilitate its detection and estimation, and to determine the part it plays in the building up of the proteid molecule. A short account of the more important of these derivatives is appended.

The *copper salt* $(C_3H_6O_2N)_2Cu,H_2O$ forms bluish-violet crystals readily soluble in water. The *nickel salt* $(C_3H_6O_2N)_2Ni,4H_2O$ forms blue crystals, these become anhydrous at 108°–110° and dissolve in 132 parts of water (Orloff, Chem. Zentr. 1897, ii. 192 ; Bruni and Formara, Atti R. Accad. Lincei, 1904, [v] 13, ii. 26). The *ethyl ester* has b.p. 48°/11 mm. and sp.gr. 0·9846 at 12·5° ; *r-alaninamide*, m.p. 62° (Franchimont and Friedman, Proc. R. Akad. Wetensch. Amsterdam, 1905, 8, 475) ; *d-alaninamide* has m.p. 72° (corr.) and $[a]_D + 6°$ in 5·2 p.c. aqueous solution ; *r-alanylchloride hydrochloride* $NH_2Cl\cdot$ $CHMe\cdot COCl$ melts and decomposes at 110° ; *d-alanylchloride hydrochloride* has $[a]_D^{20°} + 7.32$ (Fischer, Ber. 1905, 38, 605, 2914) ; *r-alanineanhydride* (*dimethyldiketopiperazine*) $NH{<}^{CHMe\cdot CO}_{CO\cdot CHMe}{>}NH$ has m.p. 282°, and *d-alanineanhydride* has m.p. 297° (corr.) and $[a]_D^{20°} -28.8°$ (Fischer, Ber. 1905, 39, 453). *Acetylalanine* $NHAc\cdot CHMe\cdot CO_2H$ crystallises in rhombic plates $a : b : c = 0.7 : 92 : 1 : 1.0983$; m.p. ·137° (de Jong, Rec. trav. chim. 19, 259 ; Fischer and Otto, Ber. 36, 2106) ; *chloracetylalanine ester* $CH_2Cl\cdot CO\cdot NH\cdot CHMe\cdot CO_2Et$ has m.p. 48·5°–49·5° (corr.) (Fischer and Otto, *l.c.*) ; the *benzenesulphonic derivative* $SO_2Ph\cdot NH\cdot CHMe\cdot CO_2H$ has m.p. 126° (Hedin, Ber. 1890, 23, 3197) ; the β-naphthalenesulphonic derivative $C_{13}H_{14}O_3NS$ melts and decomposes at 220° (Koenigs and Mylo, Ber. 1908, 41, 4427) ; for *hippurylalanine* $NHBz\cdot CH_2\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, m.p. 202°, and

derivatives, see Curtius and Lambotte, J. pr. Chem. 1904, [2] 70, 109) ; *phthalylalanine* C_6H_4: $(CO)_2 : N\cdot CHMe\cdot CO_2H$, m.p. 164°, and *phthaloylalanine* $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, H_2O, m.p. 129° (Andreasch, Monatsh. 1904, 25, 774) ; *palmityl-α-alanine* $CH_3(CH_2)_{14}\cdot CO\cdot NH\cdot$ $CHMe\cdot CO_2H$, m.p. 110°, $[a]_D^{10°} - 5.98°$ (Aberhalden and Funk, Zeitsch. physiol. Chem. 1910, 65, 61) ; *diethyldialaninquinone* $C_6H_2O_2(NH\cdot$ $CHMe\cdot CO_2Et)_2$ forms red prisms, m.p. 140° (corr.) (Fischer and Schrader, Ber. 1910, 43, 525) ; 2:4-*dinitrophenyl-d-alanine*, m.p. 178° (Abderhalden and Blumberg, Zeitsch. physiol. Chem. 1910, 65, 318).

Among the polypeptides prepared by Fischer, Abderhalden, and others, there are many containing the 'alanyl' group one or more times, *e.g. r-alanylalanine* $NH_2\cdot CHMe\cdot CO\cdot NH\cdot CHMe\cdot$ CO_2H, m.p. 276° (corr.), the *benzoyl derivative* m.p. 203°–204°, the *ethyl ester* m.p. 114°–116° ; *dialanylalanine* $NH\cdot[CHMe\cdot CO\cdot NH]_2\cdot CHMe\cdot$ CO_2H, m.p. 219° (corr.) (Fischer and Kautzsch, Ber. 1905, 38, 2375) ; *l-alanyl-d-alanine*, m.p. 269°–270° (corr.), $[a]_D^{20°} - 68.5°$; *d-alanyl-l-alanine*, m.p. 275°–276° (corr.), $[a]_D^{20°} + 68.94°$ (Fischer and Raske, Ber. 1906, 39, 2893, 3981), and the tetrapeptide *l-leucyl-triglycyl-d-alanine* decomposing at 225° (corr.), is probably a mixture of stereoisomerides of the tetrapeptide isolated from silk fibroin (Fischer, Ber. 1908, 41, 2860 ; *cf.* Abderhalden and Hirszowski, Ber. 1908, 41, 2840). For other polypeptides derived from alanine, see Fischer (Ber. 37, 2486 ; 4585 ; 38, 2375 ; 2914 ; Annalen, 340, 128, 152 ; Ber. 39, 453 ; 40, 943, 1754, 3717 ; Annalen, 363, 136), and Abderhalden (Ber. 41, 2840 ; 2857 ; 42, 3394 ; Zeitsch. physiol. Chem. 63, 401 ; 65, 417).

β-Alanine, *β-aminopropionic acid* $H_2N\cdot CH_2\cdot$ $CH_2\cdot CO_2H$, prepared by treating β-iodopropionic acid with ammonia (Mulder, Ber. 9, 1902) or with silver nitrite and reducing the resulting *nitro-* compound with tin and hydrochloric acid (Lewkowitsch, J. pr. Chem. [2] 20, 159) ; by heating ethyl acrylate with alcoholic ammonia in sealed tubes at 110° (Wender, Gazz. chim. ital. 19, 437) ; or by the action of potassium hypobromite on an alkaline solution of succinimide— this is the best method, and gives a yield of 60 p.c. of the theoretical (Hoogewerf and van Dorp, Rec. trav. chim. 10, 4 ; Holm, Arch. Pharm. 242, 590).

β-Alanine forms prisms m.p. 196° (Hoogewerf and van Dorp, *l.c.*), does not melt at 220° (Kursda, Monatsh. 12, 422), m.p. 206°–207° (Lengfeld and Stieglitz, Amer. Chem. J. 15, 504) ; the hydrochloride of the *methyl ester* has m.p. 94°–95° and of the *ethyl ester* m.p. 65·5°. The *copper salt* $Cu(C_3H_6NO_2)_2,6H_2O$ has the properties of an ordinary copper salt, and not those of a cuprammonium derivative (Callegari, Gazz. chim. ital. 1906, 36, ii. 63).

β-Alanine does not occur naturally in the body ; when administered with food it causes an increase in the urinary nitrogen, but is apparently changed with more difficulty than α-alanine, as the increased nitrogen excretion is not observed until the second day (Abderhalden and Schittenhelm, Zeitsch. physiol. Chem. 1907, 51, 323).   M. A. W.

ALANT CAMPHOR *v.* CAMPHOR.

ALANT ROOT. The root of *Inula helenium* is said to contain antiseptic principles, efficacious against tuberculosis bacilli. By distilling the root with water, *helenin, alantic acid,* and *alantol* (alant camphor) are obtained. *Alantic acid* $C_{15}H_{22}O_3$ crystallises from alcohol in white crystals, m.p. 91°; and on heating it forms the *anhydride* $C_{15}H_{20}O_2$. Both acid and anhydride are insol. in water, sol. in alcohol or fatty oils ; form sol. salts with alkalis. *Alantol* is an aromatic liquid, b.p. 200° (Marpmann, Pharm. Zent. 8, 122; J. Soc. Chem. Ind. 1887, 520).

ALBERTITE. A jet-black mineral substance resembling asphalt, discovered in 1849, at Hillsborough, Albert co., New Brunswick. Used in the United States for the production of oil and coke. The yield per ton is said to be 100 gallons of crude oil, and 14,500 cubic feet of illuminating gas, whilst a residue of good coke remains in the retorts. Albertite has been found at Strathpeffer, Ross-shire ; it contains 62 p.c. volatile matter, 37 p.c. fixed carbon, and 0·60 p.c. water. Its ultimate composition is 79·75 p.c. carbon, 8·12 p.c. hydrogen, 1·63 nitrogen, and 10·30 oxygen (Morrison, Min. Mag. 6, 101 ; Chem. Soc. Abstr. 50, 311).

ALBITE *v.* FELSPAR.

ALBUM GRÆCUM. A term formerly used for the excrement of dogs. It was at one time supposed to have medicinal properties, but is now used only for tanning, as skins treated with it, after the removal of the hair and previous to tanning, preserve their softness. It consists mainly of phosphate of lime. Fowls' dung is said by tanners to answer the purpose better.

ALBUMINOIDS and **ALBUMINS** *v.* PROTEINS.

ALCOHOL (Ethylic or Vinous), the active principle of intoxicating liquors, is, in the dehydrated condition, a colourless liquid, having a specific gravity of 0·791 at 20°/20° (Lowitz, Crell's Ann. 1796, 1, 1), 0·7938 at 15·6°/15·6° (Fownes, Phil. Trans. 1847, 249), 0·793811 at 15·6°/15·6° (Drinkwater, Phil. Mag. Feby. 1848), 0·79350 at 15·6°/15·6°, 0·79367 at 15°/4° (Mendeléeff, Pogg. 138, 230), (Squibb, Ephemeris, 1884–5, and Pharm. J. [3] 16, 147–148). It boils at 78·4° under a pressure of 760 mm. (Kopp, Annalen. 92, 9), and solidifies at −130·5° (Wroblewski and Olsewski, Compt. rend. 96, 1140 and 1225). It is inflammable, the combustion evolving great heat but little light, and producing carbon dioxide and water. It acts as a caustic irritant in contact with the tissues of the body, owing probably to the energy with which it draws moisture from the surface. It possesses a specific heat of 0·6120, at temperatures between 16° and 40·5° (Schüller, P. Erg. 5, 116–192). Its index of refraction for $H\beta=1·3667$ (Brühl), and its critical temperature 234·6° at 48·9 m. At this point 1 gram occupies 3·5 c.c. (Ramsay and Young, Proc. Roy. Soc. 38, 329).

Alcohol forms ethoxides with sodium and potassium, and unstable compounds with certain crystalline salts, *e.g.* zinc chloride, the latter called alcoholates. Subjected to the action of a limited supply of oxygen, it is converted into aldehyde (C_2H_4O), which, by further oxidation, becomes acetic acid $(C_2H_4O_2)$. Distilled with chloride of lime, it forms chloroform $(CHCl_3)$. With sulphuric acid at a temperature not ex-

ceeding 145° it yields ether $(C_4H_{10}O)$. With twice its bulk of sulphuric acid it gives ethylene (C_2H_4). With excess of dry chlorine gas it produces chloral (C_2HCl_3O).

Preparation.—Synthetically from its elements thus :—By passing an electric arc between carbon poles in an atmosphere of hydrogen, acetylene (C_2H_2) is produced, which, in the presence of nascent hydrogen, becomes ethylene (C_2H_4). Ethylene by protracted shaking with sulphuric acid is converted into sulphovinic acid, which, being distilled in presence of water, produces alcohol.

Alcohol is, for practical purposes, prepared by dehydrating the products of the distillation of fermented liquids. Up to 1796 the strongest spirit known contained not less than 5 p.c. of water. Lowitz appears to have been the first to prepare it in an approximately anhydrous condition. His process consisted in first increasing the strength of rectified spirit by adding to it dry potassium tartrate, and after decanting from this, distilling very slowly in presence of great excess of dry potassium carbonate. Richter used, instead of potassium carbonate, hot calcium chloride (Crell's Ann. 2, 211). Drinkwater first digested with dry potassium carbonate for twenty-four hours ; decanted the strong spirit thus produced, digested with as much fresh-burnt quicklime as was sufficient to absorb the whole of the alcohol, and afterwards distilled in a water-bath at a temperature of 82·2°. The product of this distillation, which was found to have a specific gravity of 0·7946 at 15·6°, was returned to the retort, and a fresh quantity of dry pulverised quicklime added to it, after which it was allowed to digest for a week at a temperature of 15·6°. It was then again slowly distilled and the specific gravity of the product found to be 0·7944 at 15·6°. This was digested at a temperature of 54·4° with hot quicklime, and distilled out of contact with the air at a temperature of 81·1° to 82·2°, and the specific gravity of the product, which was taken as absolute alcohol, found to be 0·793811 at 15·6°/15·6°.

Squibb followed the process of Drinkwater, distilling in a partial vacuum of 380 to 630 mm. The alcohol thus prepared had a specific gravity of 0·79350. The difference between this specific gravity and that found by Drinkwater represents one-tenth p.c. of alcohol. Mendeléeff's observations (Pogg. 138, 103, 230) practically confirm those of Drinkwater and Fownes.[1]

Analytical Methods.—We are dependent upon specific gravity for the exact quantitative estimation of alcohol, and perhaps no method could be devised so easy of application (*v.* ALCOHOLOMETRY). It is, however, open to the objection that it assumes water to be the only volatile substance with which the spirit is mixed, aldehyde, fusel oil, and ether when existing as impurities being reckoned as alcohol. On the other hand, no chemical method, capable of practical application, has yet been devised for the exact quantitative estimation. Berthelot's process (Compt. rend. 80, 1039) of measuring the ethylene

[1] Absolutely anhydrous alcohol produces no blue colouration with dehydrated (white) copper sulphate. It should give no cloudiness when mixed with benzene. Absolutely anhydrous alcohol added to a mixture of anthraquinone (0·001 gr.) with a little sodium amalgam gives a green colouration; if a trace of water be present the colour becomes red (Claus, Ber. 10, 927).

produced by sulphuric acid and absorbed by bromine from a given quantity of spirit is a valuable qualitative test, and within limits most useful when applied quantitatively in presence of methylic alcohol. The production of iodoform (Hager, Compt. rend. 82, 768) may be employed with advantage as a preliminary test for small quantities of alcohol, but as other bodies produce iodoform in the same circumstances, it cannot be regarded as conclusive. For the detection of alcohol in ether, Allen (Chem. Soc. Trans. 1877, 2, 930) suggests that a little fuchsine be shaken up with water and ether, and 10 c.c. of the solution thus formed agitated with the same quantity of the ether submitted for examination ; the intensity of the colour produced would be a measure of the quantity of alcohol present. For the detection of fusel oil in alcohol, Jorissen (Bied. Zentr. 1881, 791) recommends that 10 c.c. of the spirit should be mixed with 10 drops of colourless aniline and 2 or 3 drops of sulphuric acid. A deep-red colour is formed if fusel oil be present, due to the action of furfuraldehyde, an invariable constituent of fusel oil.

Alcohol is sometimes used as an adulterant in essential oils. A very ready test is to place a little of the oil in a dry test-tube, taking care in pouring it in that none adheres to the side. Rub a little fuchsine on the upper inside surface of the test-tube and apply heat, the presence of alcohol will be indicated by red stains in the fuchsine. No satisfactory method has yet been suggested for the estimation of aldehyde in alcohol, but the peculiar suffocating odour which accompanies it, and the brown colour produced by alkalis in the spirit, are indicative of its presence. A colorimetric method of estimation is generally employed by comparison of the sample with a standard solution of aldehyde, using Schiff's reagent.

Manufacture.—The first process in the manufacture of spirit is one of brewing, and in general principles it does not differ from that employed in making beer. The brewer, as well as the distiller, endeavours to treat his materials in such a way as to extract from them the greatest amount of fermentable matters. The brewer of beer, however, does not desire to convert all the matter he extracts into spirit, and he brews at such gravities as his customers require. The distiller desires to convert as much as possible of the matter he has extracted from his materials into spirit ; he therefore produces a wort containing more maltose and less dextrinous matter than the brewer of beer. He has also an advantage over the brewer in being able to choose the gravities which he knows by experience will produce the best results. It has been found that for distillers' purposes it is advisable to keep the specific gravity of the wort when set for fermentation below 1040. The principle of low temperatures when the diastase is acting in the mash tun appears to be fully recognised, 60° to 63° being generally adopted, and it is understood that the higher the temperature at which the worts are set for fermentation, the greater is the amount of fusel oil in the spirit. The distiller has, therefore, to choose the lowest temperature at which a healthy fermentation can be started, and this is found to range between 23° and 25°. He cannot be too careful as to the purity of the

yeast, for not only has he to run the risk of acetic and other ferments being introduced into the wort, involving loss of alcohol, but to provide against the presence of aldehyde, which is objectionable in the spirit. Kekulé attributes the presence of aldehyde to the action of nitrates derived from the materials. It is found in practice that it is always more prone to appear in hot weather, when the difficulty of keeping the yeast from decomposition is greatest, and as yeast always contains some spirit in a dilute form it is not improbable that the aldehyde is frequently a product of the oxidation of this spirit.

The materials used in the manufacture of alcohol in the United Kingdom are chiefly malt, maize, rice, sago, tapioca, barley, rye, oats, sugar, and molasses, but occasionally dates and locust beans have been employed. At the present time *maize* constitutes fully 75 p.c. of the grain used. In Scotland the smaller distillers use malt only, and the spirit they produce under the name of Highland, Campbeltown, or Islay Whiskey, Glenlivet, Lochnagar, &c., has imparted to it a flavour derived partly from the peat used in drying the malt. The process of manufacture consists in distilling the fermented wort—then called wash—in a common still, collecting the distillate, which is weak spirit contaminated with fusel oil, and is called 'low wines,' and redistilling. The spirit which passes over in the middle of the redistillation is that which is used for consumption. It contains from 60·8 to 76·7 p.c. of alcohol by weight (20 overproof to 45 overproof), but is generally diluted by the addition of water to 55·4 p.c. of alcohol by weight (11 overproof) before being sent into consumption or placed in bond. Irish whiskey differs from Scotch chiefly in the absence of peat flavour. The materials used in its manufacture are, with one or two exceptions, a mixture of malt and grain, the proportion of malt being, however, greater than in English distilleries. It is generally bonded at 25 overproof (64 p.c. of alcohol by weight).

We have hitherto dealt with the spirit manufactured in 'Common' or 'Pot' stills, or in other words by boiling the wash, condensing the steam thus produced, reboiling the product and recondensing. But by far the greater quantity of the alcohol of commerce is produced by the Coffey still, in which the alcoholic vapour produced is deprived of water as the process continues until a spirit is formed of much greater purity than that manufactured by the old method. The annexed illustration represents a Coffey's distilling apparatus, the left-hand column being called the *analyser*, the right hand one the *rectifier*. The first operation is to fill both columns with steam. This is accomplished by introducing it under pressure from the boiler at C, whence it ascends within the analyser, passing by the pipe M into the bottom of the rectifier. When a proper temperature has been attained, the wash is pumped from the wash charger by a pipe which enters the top of the rectifier. This pipe is only shown sectionally in the sketch after entering the column, but it is continuous, and the wash passes slowly through it, becoming warmer, owing to the pipe being in contact with the steam. When it has reached the bottom of the

rectifier it is not far from the boiling-point. It will be seen that the pipe then ascends, and finally delivers the wash into the top of the analyser. The lines across the analyser represent plates of perforated copper, and in connection with each is a tube which projects about an inch and a half above the plate, and dips into a
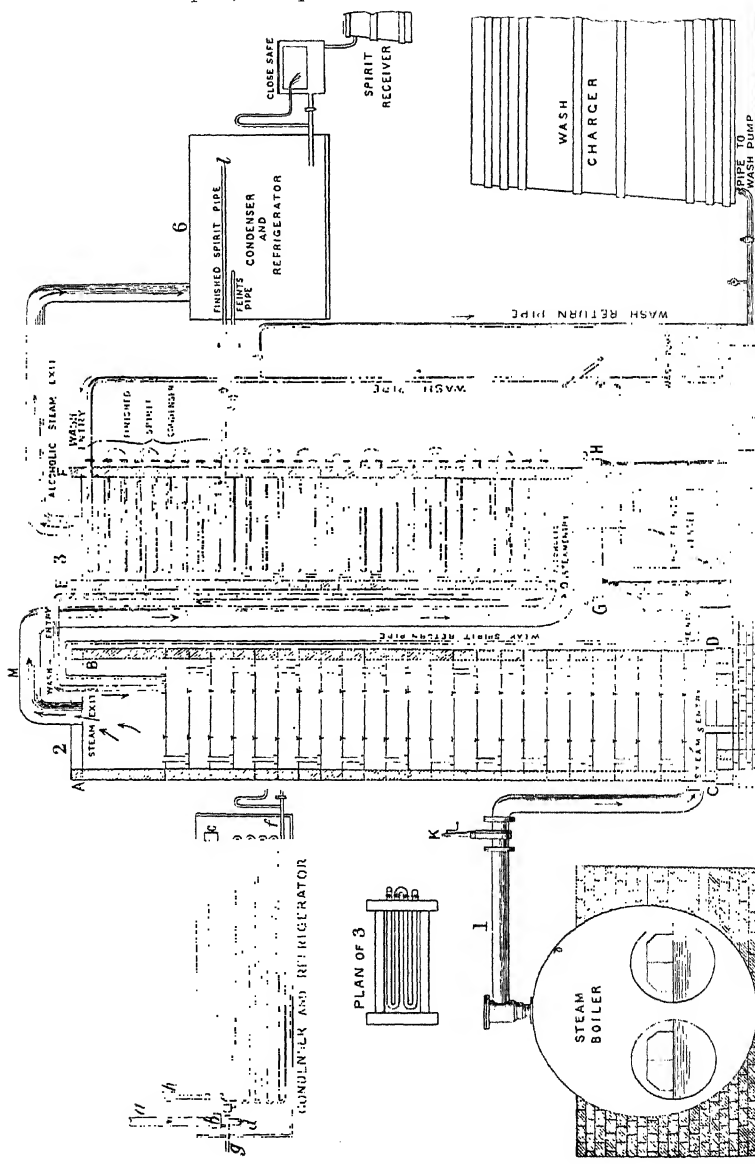
pipe, so that by the time the wash has reached the bottom of the column it has been deprived of its alcohol. The alcoholic vapour passes by the pipe M into the bottom of the rectifier, which like the analyser contains plates and metal tubes, and where a process of gradual cooling takes place by the action of the pipe carrying the cold wash. Fusel oil vapour, condensing at a higher temperature than alcohol, is the first to assume the liquid form, and contaminated with spirit passes into the hot ' feints ' receiver. The vapour containing alcohol continues to ascend, meeting with portions that have condensed, and are undergoing the process of rectification. It will be seen that the upper part of the apparatus is marked off in the sketch as finished-spirit condenser. It is so called because all that condenses within its area, instead of returning towards the bottom of the apparatus to be rectified, passes by the finished-spirit pipe or feints pipe into the receivers. At the top of the apparatus is a pipe marked ' alcoholic steam exit,' which carries away most of the aldehyde as well as spirit vapour which under special circumstances may not have been condensed before reaching that point.

The English distillers confine themselves almost exclusively to this apparatus, brewing for the most part from a mixture of grain and malt. In addition to Coffey's still, various forms of rectifying stills are in use to meet special requirements, e.g. the production of a purer though not stronger spirit than that obtainable from the Coffey still for the purpose of compounders and certain manufacturing processes, and apparatus having for their object (in consequence of the increasing demand for fusel oil) the recovery of the maximum amount of this by-product, which indeed is now considerably more valuable than the spirit itself. The spirit produced does not to any large extent go into consumption as whiskey, the want of flavour being an objection in regard to the better qualities. Large quantities are transferred to the rectifiers, who redistil them with various flavouring ingredients, producing gin, British brandy, British rum, and the various cordials. A portion after being redistilled from potash or potassium carbonate, or filtered through charcoal, is used in the arts and in medicine under the names of rectified spirit and spirits of wine. The British Pharmacopœia (1898) requires rectified spirit to be of a specific gravity of 0·834, equal to 85·65 p.c. of alcohol by weight. The Pharmacopœia of the United States fixes it at 0·820, equal to 91 p.c.,which is about the strength it comes from Coffey's apparatus. It is from this spirit that anhydrous or absolute alcohol is generally prepared. It varies considerably in flavour, and, according to the United States Dispensatory, 1883, the purest is produced under Atwood's patent, in which permanganic acid is used to destroy the disagreeable organic substances. It has been suggested that the purity of strong spirit might be considerably increased by redistilling *in vacuo*. Reference has already been made to the occurrence in variable quantity of secondary products on fermentation. Pasteur (Ann. Chim. Phys. 58, 330) showed that on the fermentation of sugar 3·16 p.c. of glycerol and 0·67 p.c. of succinic acid are produced. These bodies are, however, very slightly volatile, and

therefore can only pass into the spirit in very small proportion.

We have hitherto only dealt with spirits manufactured in the United Kingdom. Of the more important foreign spirits, the principal is brandy, the production of which from grape wine is an industry confined almost entirely to France. The best brandy is derived from white wine, but a considerable quantity of spirit is imported from the Continent under the name of brandy, which has either been mixed with other spirits or prepared from substances bearing no relation to wine. The distillation of genuine brandy takes place in stills which are practically on the pattern of common or pot still's ; the improvements being chiefly confined to the adoption of means for carrying on the distillations continuously. Illustrations of the various stills now in use will be found in Duplais' treatise on the manufacture and distillation of alcohol. Brandy is generally imported into this country at a strength a little below proof (47 to 48 p.c. of alcohol by weight) (*v.* BRANDY).

Rum is the spirit produced by fermenting diluted molasses and distilling the product in an ordinary still. Its character is due to the formation of ethyl butyrate, which, when added to other spirits, produces a flavour difficult to distinguish from genuine rum. The strength at which rum is generally imported into this country is about 35 overproof (70 p.c. of alcohol by weight) (*v.* RUM).

The molasses from the beet-sugar manufactories in France is now utilised in making spirit, being simply neutralised, generally mixed with a little rye flour and malt, fermented and distilled. The best qualities of spirits thus produced are devoid of taste or any peculiar aroma, and are employed in the manufacture of liqueurs, for improving common brandies, and for refining rectified spirit.

Geneva or Hollands is a well-known form of gin manufactured in Holland, where the grain spirit is for the most part made from a mixture of malt and rye. It does not possess any characteristic to distinguish it from the same article manufactured by rectifiers in this country, and its consumption appears to be declining (*v.* GIN). Absinth is a form of gin in which the spirit is flavoured with the bitter principle of wormwood, together with extracts of some or all of the following plants : fennel, hyssop, anise coriander, angelica seed, dried veronica, chamomile, and mint (*v.* ABSINTH). A large quantity of spirit manufactured in Germany from potatoes is imported into this country, coming into competition with the lowest qualities of spirits of wine of the British distilleries.

Reference has already been made to the bonding of whiskey—that is, placing it in warehouses under the control of the revenue authorities, where it remains maturing for periods varying from a few months to several years. The exact change which takes place during the maturing process has not yet been satisfactorily explained, although the labours of Pelletan, Dumas and Stas, Gaultier, Chancel, Wurtz, Cahours, Balard, Liebig and Pelouze, Pasteur, Fittig, and Krämer and Pinner have added largely to our knowledge of the subject. According to the researches of these authorities fusel oil is a complex

substance and a necessary accompaniment to fermentation. In grain fermentations amyl alcohol is the predominant constituent of this oil, but propyl and butyl alcohol are also present. In wine fermentations it consists principally of œnanthyl and caproyl alcohols. It is probable that these alcohols are converted, in the process of maturing the spirit, from a disagreeable-smelling and highly intoxicating body into compound ethers which are both fragrant and harmless.

In the process of mellowing there is generally a loss of alcohol, varying with the length of time and the condition of the atmosphere of the warehouse. The revenue authorities fully recognise this, and make the necessary allowances in charging the duty. It will therefore be apparent that alcoholic strength based on specific gravity is not always a measure of the money value of spirits as beverages. The Food and Drugs Amendment Act (42 & 43 Vict. c. 30) has fixed a limit below which spirits shall be assumed to be diluted. This limit is 25 under proof (35·8 p.c. of alcohol by weight) for whiskey, brandy, and rum; and 35 under proof (30·8 p.c. alcohol by weight) for gin.

Uses.—In addition to its use as a beverage, spirit is employed as a solvent for many of the drugs required in medicine, and diluted to the standard of British proof—that is, to the specific gravity of 0·91984 at 15·6°, representing 49·24 p.c. by weight of Drinkwater and Fownes alcohol—it forms part of a large proportion of the tinctures of the Materia Medica. It is also used largely as a solvent for essential oils, in preparing perfumes and essences, and ether is manufactured from it. The alcohol used in all the above preparations pays a duty of 15s. 1d. per proof gallon, equal to about 27s. per gallon of the alcohol of Gay-Lussac, the standard of France.

Adulteration.—Although it has been stated that spirits, especially gin, were formerly adulterated with capsicum and even sulphuric acid, in order to increase their fiery character, it is satisfactory to find that in the working of the Food and Drugs Act no evidence has been afforded of such practices during late years. The report of the Local Government Board (1909) shows that the adulterants detected during the year consisted of water (the great majority of cases); foreign spirit in 16 samples out of 5217 samples of brandy, rum, and whiskey examined; one case (whiskey) contained an admixture of sherry wine.

Methylated spirit. In 1853 a strong representation was made to the Government to allow the use of alcohol duty free in the arts and manufacturing processes in which it was required, and after careful inquiry the Board of Inland Revenue in 1855 decided to sanction, under certain restrictions, a mixture of nine parts of spirits of wine and one part of methyl alcohol (wood naphtha) free of duty under the name of *methylated spirits.* In 1861 the permission was extended to all other purposes except consumption as a beverage or as a medicine. The reasons for selecting wood naphtha were that whilst it would be least likely to interfere in any of the processes for which alcohol was required—especially as a solvent—it would be very difficult to separate from the alcohol when once mixed.

The principal restriction on the use of methylated spirit is that it shall only be kept by authorised persons and in authorised premises.

In 1891 it was found necessary (owing to the possibility of methylated spirit being sufficiently purified to render it fit for potable purposes, and the growing practice of drinking even the unpurified methylated spirit by the poorer classes in some of the larger cities) to again restrict the use of methylated spirit made as above described (*i.e.* ' ordinary methylated spirit ') to manufacturers only, and, even then, subject to revenue restrictions, and to prescribe the addition of a further denaturant to methylated spirit intended for general purposes. This denaturant consists of mineral naphtha (petroleum), and the mixture, known as ' *mineralised*' methylated spirit, may be sold by licensed retailers to the general public for any purpose to which it is applicable, as lighting, heating, cleansing, or mixing with paints, varnishes, &c.

It was found, however, that ' ordinary ' methylated spirit was not universally applicable to manufacturing processes requiring the use of alcohol, and accordingly, in 1902, the Commissioners of Inland Revenue, under powers conferred upon them by the Spirits Act of 1880 and the Finance Act of 1902, authorised the use of duty-free alcohol denatured with substances other than wood-naphtha in certain manufacturing operations and subject to special conditions.

As the result of an inquiry by a Departmental Committee, in 1904–5, the amount of wood-naphtha to be used as a denaturant for ' ordinary ' methylated spirit used for industrial purposes was reduced from 10 to 5 p.c. of the mixture. This is described as ' *industrial*' *methylated spirit.*

At the present time (1911), there are, therefore, two descriptions of methylated spirit officially recognised in the United Kingdom, viz. :

(*a*) *Mineralised methylated spirit* as sold by licensed retailers for general use (except for the preparation of beverages or medicine), and containing not less than 10 p.c. by volume of approved wood-naphtha, and, in addition, not less than 0·385 p.c. of approved mineral naphtha (petroleum of specific gravity not less than 0·800).

(*b*) *Industrial methylated spirit,* intended for use in manufacturing processes, and sold only by methylators to persons authorised to receive this kind of spirit. This must contain not less than 5 p.c. of approved wood-naphtha or other substance or combination of substances approved by the Commissioners of Customs and Excise.

The wood-naphtha must be sufficiently impure to make the methylated spirits so nauseous as to render them incapable of being used as a beverage or of being mixed with potable spirits without rendering them unfit for human consumption. It must contain not less than 72 p.c. by volume of methyl alcohol, and not more than 12 grams per 100 c.c. of aldehydes, acetone, and higher ketones, estimated as acetone by Messinger's iodoform process, nor more than 3 grams of esters estimated as methyl acetate by hydrolysis; not more than 30 c.c. of naphtha shall be required to decolourise an aqueous solution containing 0·5 gram of bromine, and 5 c.c. at least of deci-normal acid shall be required to neutralise 25 c.c. of the spirit when methyl orange is used as indicator.

The wood-naphtha which is now used by methylators is fairly uniform in character as regards its content of methyl alcohol, and it is by the recognition of this alcohol that the presence of methylated spirits is usually detected. Acetone is present in much more varying quantities, whilst unsaturated alcohols, compound ethers, and nitrogenous basic substances are present in too small and varying proportions to afford suitable means for dectecting methylated spirits in mixtures.

The most satisfactory methods for detecting methyl alcohol in presence of ethyl alcohol depend either on differences in the physical properties of the alcohols themselves, or on differences in the chemical behaviour of their derivatives or products of oxidation, but of these, few are capable of indicating with certainty the presence of less than 1 p.c. of methyl alcohol.

Of the methods which have hitherto been devised for this purpose, none can compare, as regards the certainty of the conclusions which may be drawn from the results, with that of Riche and Bardy, which depends on the ultimate formation of methylaniline violet and its deposition on merino-wool (Compt. rend. 1875, 1076). As a preliminary test, and one which may with advantage be incorporated in the Riche and Bardy process, the following will be found to be useful. About 10 c.c. of the strong spirit—freed, if necessary, from essential oils, &c., by the salt-petroleum method and fractionated (v. ALCOHOLMETRY)—are placed with 30 grams of powdered iodine in a small round-bottomed flask which can be readily connected with a condenser. Two grams of amorphous phosphorus are added and the resulting alkyl iodides distilled and collected under water in a small separator. When from 10 to 12 c.c. have been collected, the iodides are washed with water, decolourised with dilute potash, and drawn off from the aqueous layer into a flask containing a little freshly heated potassium carbonate. After remaining an hour or so with occasional shaking, the potassium carbonate is removed by filtration, and the boiling-point of the iodides carefully determined. Ordinary ethyl alcohol yields an iodide which has a constant boiling-point of 72°. When methyl alcohol is present in the spirit, the initial boiling-point of the iodides is lower and a portion distils below this temperature. By noting the temperature at which the first drop of distilled iodides falls into the condenser and receiver respectively, the presence of relatively small quantities of methyl alcohol can be detected. The results (see table in next col.) obtained with synthetic mixtures indicate the delicacy of the method.

In doubtful cases, or when the initial boiling-point is below 70°, the first fraction of 3 c.c. of distilled iodides is digested with an equal volume of aniline at a moderate temperature, and the Riche and Bardy method proceeded with. After standing one hour, hot water is added to the crystalline mass, and the mixture boiled for some minutes, 25 c.c. of strong potash solution are then added, and the liberated aniline oil washed with water; 1 c.c. of this oil is intimately mixed with 10 grams of a mixture consisting of 100 grams of dry quartz sand, 3 grams of cupric nitrate, and 2 grams of

common salt, and the mixture introduced into wide tube and heated for some hours at 90°–100°. The product is exhausted with warm alcohol and the extract filtered and made up to volume of 100 c.c.

If the sample of spirit contained ethyl alcohol only, the colour of the liquid will be red, but in the presence of 1 p.c. of methyl alcohol it has a distinct violet shade, whilst in the presence of 2 p.c. the violet is very decided, and becomes more so as the proportion of

Percentage of methyl alcohol by volume in the mixture of alcohols	Temperature at which the first drop of iodides falls into the condenser	Volume of distillate obtained below 72° from 10 c.c. of iodides
		c.c.
Nil	70°	Nil
0·38	69°	0·2
0·94	65°	0·8
1·86	63°	2·2
2·77	62°	4·0
3·66	60°	5·0
4·55	58°	6·0
5·42	57°	6·2
6·26	56°	6·4
7·10	55°	6·5
10·00	52°	7·5

methyl alcohol increases. 5 c.c. of the alcoholic extract are then mixed with water to a volume of 100 c.c., and 2 c.c. of this dye diluted with water to about 400 c.c. The mixture is now heated to a temperature not exceeding 75°, and from two to three feet of Berlin wool, previously freed from grease by treatment with hot dilute potash, immersed in it for 30 minutes. Pure ethyl alcohol under these conditions will not produce a dye, and the wool after washing and drying remains practically white. If, however, methyl alcohol was originally present, the fibre will be violet, the tint becoming more intense and increasing in depth according to the quantity present. Riche and Bardy recommend that 5 c.c. of the above diluted dye should be taken instead of 2 c.c. as here described, but although by this means a more intense dye is obtained when methyl alcohol is present, it is found that an appreciable dye, although not of the same colour, is deposited when pure ethyl alcohol has been operated with, and this may lead to confusion. For purposes of comparison it is therefore advisable to operate concurrently with a sample of rectified spirits.

If it be desired to estimate the proportion of methyl alcohol or methylated spirits in a sample, the method of Thorpe and Holmes may be employed. This method depends on the complete oxidation of methyl alcohol to carbon dioxide by means of chromic acid mixture, rectified spirits under the same conditions yielding only a small quantity of carbon dioxide equivalent to 0·01 gram for each gram of ethyl alcohol present (Chem. Soc. Trans. 1904, 1).

As a result of many experiments it has been proved that unless the boiling-point of the iodides is abnormal, no dye is obtained by the Riche and Bardy method, nor does the yield of carbon dioxide on oxidation exceed the limits

given above for rectified spirits, but in all cases in which a dye is obtained a proportional excess of carbon dioxide is also obtained.

In other countries there are, as a rule, classes of denatured alcohol corresponding more or less with those authorised in the United Kingdom, *i.e.* spirit for general use so completely denatured as to be deemed undrinkable, and spirit not absolutely denatured and intended for use by responsible manufacturers subject to a more or less strict revenue control.

Wood-naphtha is the denaturant most in favour for spirit intended for general use, the nauseous character of the methylated spirit being sometimes intensified by the addition of such substances as pyridine bases, benzine, &c.

In *France*, spirit for general use contains one-eleventh of its volume of officially approved wood-naphtha, with an addition (when used for lighting and heating purposes) of 0·5 p.c. of heavy benzine distilling between 150° and 200° and 4 p.c. of gum resin for ' finish.'

In *Germany*, the official formula is 2 p.c. of wood naphtha, 0·5 p.c. of pyridine bases, and (optionally) 0·125 p.c. of rosemary oil. Spirit intended for motor cars, and internal combustion engines is denatured by adding 1 p.c. of wood-naphtha, 0·25 p.c. of pyridine bases, 0·25 p.c. of a solution of methyl violet dye, and from 2 to 20 p.c. of benzol to the pure spirit.

In the *United States of America*, 10 p.c. of approved methyl alcohol and 0·5 p.c. of benzene is prescribed to be added to spirit denatured for general use.

Austria-Hungary: Two p.c. of wood-naphtha, 0·5 p.c. of pyridine bases, and a trace of phenol phthalein are added to spirit intended for general purposes.

In *Belgium* and *Russia* specific denaturants are prescribed for each of the principal manufacturers, and this practice obtains in certain other countries, as Germany, France, Switzerland, and the United Kingdom, when it can be shown that ordinary methylated spirit is unsuitable. In such cases the denaturants are naturally very varied in character, being specially adapted to the particular necessities of each manufacturer.

(Minutes of Evidence and Report of the Departmental Committee on Industrial Alcohol, 1905 ; Herrick, Denatured or Industrial Alcohol.)

ALCOHOLOMETRY is the term applied to any process for estimating the amount of alcohol in a spirituous liquid. In simple mixtures of alcohol and water a determination of specific gravity at a standard temperature affords an accurate index of alcoholic content, and it is by taking advantage of this fact that the assay of spirit for revenue and commercial purposes is usually carried out.

When alcohol and water are mixed together the volume of the mixture is invariably less than the sum of the initial volumes, and the degree of contraction varies with the proportion of alcohol present. In countries in which the revenue from spirit is of great importance it has therefore been found necessary to ascertain by experiment the specific gravities of mixtures of alcohol and water in all proportions and at various temperatures. These experiments have in general been carried out at the request of the Governments interested, and the results are

embodied in tables associated with the names of those entrusted with the investigations.

In 1794 Sir Charles Blagden and Mr. Gilpin completed an extensive series of experiments, undertaken at the request of the British Government (Phil. Trans. 1790–1794), the results of which have since served as the basis of systems of alcoholometry in this and other countries. At that time anhydrous alcohol had not been prepared, Blagden and Gilpin's tables having reference to spirit of a sp. gr. 0·825 at 15·6°/15·6° (60°/60°F.). Tralles, in 1811, conducted a like investigation for the Prussian Government (Gilb. Ann. 1811), and adopted 0·7946 as the specific gravity of alcohol at 15·6°/15·6°. He incidentally confirmed the general accuracy of the results of Blagden and Gilpin, and constructed tables of spirit-strengths which for upwards of sixty years formed the basis of German alcoholometry. Similar researches were undertaken by Gay-Lussac (Paris, 1824), McCulloch (Washington, 1848), Baumhauer (Amsterdam, 1860), Mendeléeff (St. Petersburg, 1865), and more recently by the Kaiserliche Normal Eichungs Kommission (Berlin, 1889), the several results of which have from time to time been incorporated in the systems of alcoholometry adopted by the respective Governments. The unofficial investigations of Fownes (Phil. Trans. 1847), Drinkwater (Chem. Soc. Mem. 1848), and Squibb (Ephemeris, 1884), are likewise entitled to consideration.

Drinkwater prepared alcohol of a specific gravity 0·79381 at 15·6°/15·6° (in air), whilst Squibb obtained it as low as 0·7935, but this result lacks confirmation.

The work of Mendeléeff for the Russian Government admittedly constitutes the most comprehensive and exact of the researches hitherto made in the field of alcoholometry. Mendeléeff obtained alcohol of a specific gravity 0·79425 at 15°/15°, which at 15·6°/15·6° is equivalent to 0·79384 in a vacuum, or to 0·79359 in air, and he assigned to Drinkwater's alcohol an alcoholic content of 99·95 p.c., and to the strong spirit of Blagden and Gilpin 89·06 p.c. by weight. The results of Tralles' and Gay-Lussac's experiments, being based on alcohol less dehydrated than that of Drinkwater, compare less favourably with those of Mendeléeff.

Mendeléeff was so well satisfied with the work of Blagden and Gilpin, and Drinkwater, that, for spirituous mixtures of low strength, he included many of their results in his tables of spirit-densities, and after a critical investigation and subsequent verification by the Kaiserliche Normal Eichungs Kommission, his results have been substantially adopted as the basis of the present system of German alcoholometry in place of the relatively less accurate data of Tralles.

The results of the work of these four authorities have been incorporated in the accompanying table of spirit-densities, which may serve for the pyknometrical determination of the true strength of spirits. In the assessment of duty and in commercial transactions, the standard of strength is termed ' proof.' Spirit of proof strength is defined as ' that which at the temperature of 51°F. (10·6°C.) weighs exactly ¹²⁄₁₃ths of an equal measure of distilled water ' also at 10·6°. According to the best available data this mixture of alcohol and water has a specific gravity of 0·91976 at 15·6°/15·6°, and contains

Specific gravity in air at 15·6°	Percentage of alcohol		Percentage of fiscal proof spirit	Specific gravity in air at 15·6°	Percentage of alcohol		Percentage of fiscal proof spirit
	by weight	by volume at 15·6°			by weight	by volume at 15·6°	
0·79359	100·00	100·00	175·35	0·898	58·93	66·67	116·81
0·794	99·87	99·92	175·21	0·900	58·06	65·83	115·33
0·796	99·22	99·52	174·52	0·902	57·18	64·98	113·84
0·798	98·57	99·12	173·80	0·904	56·31	64·13	112·35
0·800	97·91	98·70	173·07	0·906	55·42	63·26	110·82
0·802	97·25	98·28	172·33	0·908	54·54	62·39	109·29
0·804	96·57	97·84	171·56	0·910	53·65	61·51	107·74
0·806	95·89	97·39	170·77	0·912	52·77	60·63	106·20
0·808	95·20	96·93	169·96	0·914	51·88	59·74	104·63
0·810	94·50	96·45	169·13	0·916	50·98	58·83	103·05
0·812	93·80	95·97	168·28	0·918	50·08	57·92	101·43
0·814	93·08	95·47	167·41	0·91976	49·28	57·10	100·00
0·816	92·36	94·97	166·51	0·920	49·17	56·99	99·80
0·818	91·63	94·45	165·60	0·922	48·25	56·05	98·16
0·820	90·90	93·92	164·67	0·924	47·33	55·10	96·49
0·822	90·16	93·38	163·72	0·926	46·40	54·14	94·80
0·824	89·41	92·83	162·75	0·928	45·47	53·16	93·09
0·826	88·65	92·26	161·76	0·930	44·53	52·18	91·36
0·828	87·88	91·69	160·75	0·932	43·59	51·18	89·61
0·830	87·11	91·11	159·73	0·934	42·62	50·15	87·81
0·832	86·34	90·52	158·69	0·936	41·64	49·10	85·97
0·834	85·56	89·91	157·63	0·938	40·65	48·04	84·10
0·836	84·78	89·30	156·56	0·940	39·65	46·95	82·19
0·838	83·99	88·68	155·47	0·942	38·64	45·85	80·26
0·840	83·20	88·06	154·37	0·944	37·60	44·71	78·26
0·842	82·40	87·42	153·25	0·946	36·54	43·54	76·21
0·844	81·60	86·77	152·12	0·948	35·46	42·35	74·12
0·846	80·79	86·12	150·97	0·950	34·37	41·13	71·98
0·848	79·98	85·46	149·80	0·952	33·25	39·87	69·76
0·850	79·17	84·78	148·62	0·954	32·09	38·57	67·48
0·852	78·35	84·11	147·43	0·956	30·90	37·20	65·09
0·854	77·53	83·42	146·23	0·958	29·66	35·79	62·60
0·856	76·71	82·73	145·01	0·960	28·39	34·33	60·03
0·858	75·88	82·03	143·78	0·962	27·06	32·79	57·33
0·860	75·05	81·32	142·54	0·964	25·68	31·18	54·51
0·862	74·22	80·61	141·28	0·966	24·23	29·48	51·53
0·864	73·39	79·89	140·22	0·968	22·71	27·69	48·38
0·866	72·55	79·16	138·74	0·970	21·14	25·83	45·14
0·868	71·72	78·43	137·46	0·972	19·53	23·91	41·77
0·870	70·88	77·69	136·16	0·974	17·90	21·96	38·35
0·872	70·04	76·94	134·84	0·976	16·25	19·98	34·87
0·874	69·19	76·19	133·53	0·978	14·61	18·00	31·42
0·876	68·35	75·44	132·19	0·980	12·99	16·04	27·99
0·878	67·51	74·68	130·86	0·982	11·42	14·13	24·66
0·880	66·66	73·91	129·50	0·984	9·91	12·29	21·44
0·882	65·81	73·13	128·14	0·986	8·46	10·51	18·34
0·884	64·96	72·34	126·77	0·988	7·08	8·80	15·38
0·886	64·10	71·55	125·37	0·990	5·76	7·18	12·53
0·888	63·24	70·75	123·97	0·992	4·51	5·63	9·82
0·890	62·38	69·95	122·56	0·994	3·31	4·14	7·24
0·892	61·52	69·14	121·14	0·996	2·17	2·71	4·73
0·894	60·66	68·33	119·70	0·998	1·07	1·34	2·33
0·896	59·80	67·50	118·26	1·00000	0·00	0·00	0·00

49·28 p.c. by weight and 57·10 p.c. by volume of anhydrous alcohol. Spirits which contain a greater proportion of alcohol than is contained in proof spirit are said to be of overproof strength (o.p.), and those which contain a smaller proportion are said to be of underproof strength (u.p.). Variations of temperature are deemed not to affect the fiscal strength of spirits. Spirits which are of proof strength at 10·6° are consequently deemed to be of proof strength at other temperatures, and the same applies to spirits of any other strength, provided that no change in composition has occurred. In computing the strength of a spirit mixture reference is made to the volume of proof spirit it contains, if underproof, or will produce if overproof, at the dominant temperature, which for revenue purposes in this country is fixed at 10° (50°F.). Mendeléeff's alcohol is thus found to be 75·35 overproof, or 100 volumes at 10°, when diluted

leaving the carbon behind. This, when carefully washed and dried, forms a most valuable decolourising agent.   N. BROS.

ANIMAL OILS and **FATS** v. OILS AND FATS.

ANIME and **ANIMI** v. OLEO-RESINS.

ANISEED. (*Anis*, Fr., Ger.) The fruit of the *Pimpinella Anisum* (Linn.), cultivated in Malta, Spain, and Germany. Used for the preparation of anise oil and cordials. Alcohol extracts 36·24 p.c. of this spice (Biechele, Pharm. J. [3] 10, 878).

ANISE CAMPHOR v. CAMPHORS.

ANISE OIL. The essential oil of aniseed, obtained by distilling it with water. According to Landolph (Compt. rend. 81, 97 ; 82, 226), it contains 90 p.c. of *anethole*, boiling at 226°. Anethole, according to Perkin (Chem. Soc. Trans. 32, 668), is *p*-allylanisole $C_6H_4(OMe)CH : CH·CH_3$; he obtained it by heating *p*-methoxyphenylcrotonic acid.

Anise oil is sometimes adulterated with fennel oil ; this can be detected by heating the oil, when the fennel odour becomes perceptible.

Star anise oil has a similar colour and taste, but it does not solidify at 2° (v. OILS, ESSENTIAL).

ANISIDINE. $NH_2·C_6H_4·OMe.$ *Orthanisidine.* Obtained by the reduction of orthonitranisole with tin and hydrochloric acid or iron and hydrochloric acid (Meister, Lucius, and Bruning, D. R. P. 7217 of Dec. 3. 1878), is a colourless oil, which boils at 226·5° at 734 mm. pressure (Mühlhaüser, Annalen, 207, 239) ; at 225° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210), and has a sp.gr. 1·108 at 0°. When diazotised and treated with β-naphtholdisulphonic acid (R-acid), it yields *anisole-red* (v. AZO- COLOURING MATTERS). A mixture of orthanisidine (2 mols.) and paraphenylenediamine (1 mol.) is converted, on oxidation with potassium dichromate, into a reddish colouring matter formerly employed under the name *safranisole* (Kalle & Co., D. R. P. 24229 of Oct. 27, 1882 ; expired March, 1885).

Paranisidine, obtained from paranitranisole by reduction with tin and hydrochloric acid, crystallises in prisms which melt at 55·5°–56·5° (Lossen, Annalen, 175, 324) and boil at 245°–246° (Salkowski, Ber. 7, 1009) ; 243° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210) ; *p*-anisidine, *o*-sulphonic acid, prepared by boiling the hydrogen sulphate of *p*-anisidine, when diazotised and coupled with β-naphthol, yields an azo-compound forming red lakes with baryta, alumina, &c. (Aktiengesellschaft für Anilin-Fabrikation, D. R. P. 14665).

Chloranisidine, when diazotised and coupled with β-naphthol, yields a red compound insoluble in water (Julius, Ludwigshafen and Jahrmaht, U.S. Pat. 695812) ; *p*- and *m*-nitroanisidine, when diazotised and coupled with β-naphthol, yield red and pink dyestuffs (Imray, Eng. Pat. 25756 ; J. Soc. Chem. Ind. 1898, 1039 ; and Freyss, J. Soc. Chem. Ind. 1901, 356) ; *o*-iodo-*p*-anisidine, when diazotised and treated with naphthol sulphonic acid, yields a red dye, similar to that obtained from *p*-anisidine (Reverdin, Ber. 29, 997).

Anisidine condenses with orthoformic ester, and the resulting compound is used as an anæsthetic (Goldchsmidt, Eng. Pat. 9792 ; J. Soc. Chem. Ind. 1899, 606).

ANISOCHILUS CARNOSUS (Wall.). An Indian plant belonging to the Labiatæ and containing a volatile oil. Used in quinsy.

ANISOLE. *Anisoil ; Methylphenyl ether*
$$C_6H_5·O·CH_3.$$

Preparation.—Anisole can be obtained by distilling anisic acid or *o*-methoxybenzoic acid with baryta, or by heating potassium phenate with methyl iodide at 120° (Cahours, Ann. Chim. Phys. [3] 2, 274 ; 10, 353 ; 27, 439). It is prepared by passing a current of methyl chloride over dry sodium phenate heated at 190°–200° (Vincent, Bull. Soc. Chim. 40, 106), and by heating phenol with methyl alcohol and potassium bisulphate at 150°–160° (Act. Ges. für Anil.-Fabrik.; D. R. P. 23775). It has been synthesised by fusing sodium benzene sulphonate with sodium methoxide (Moureu, J. Pharm. Chim. 8, v. 211).

Properties.—It is a colourless ethereal liquid, which boils at 155°–155·5° at 762·3 mm. (Schiff, Annalen, 220, 105) at 153·9° (corr.) (Perkin, Chem. Soc. Trans. 69, 1240) ; melts at − 37·8° (Von Schneider, Zeit. Phys. Chem. 19, 997) and has a specific gravity 0·991 at 15° (v. OILS, ESSENTIAL).

ANISOMELES MALABARICA (R. Br.). A much-esteemed Indian plant belonging to the Labiatæ ; an infusion of the leaves is used in intermittent fevers, and the essential oil is applied externally in rheumatism.

ANKOOL, AKOLA, DHERA BARK. The root bark of *Alangium Lamarckii* (Thw.), one of the Cornaceæ, used in leprosy and skin-diseases (Dymock, Pharm. J. [3] 9, 1017).

ANNATTO is derived from the fruit of the *Bixa orellana* (Linn.), a shrub found native in Central America, and cultivated in Brazil, Guiana, Mexico, the Antilles, and India.

To prepare the dyestuff, the seeds and pulp are removed from the mature fruit, macerated with water, and the mixture is left to ferment. The product is strained through a sieve, and the colouring matter which settles out is collected, partially evaporated by heat, then placed in boxes, and finally dried in the sun.

Annatto comes into the market in the form of cakes, and, among the different varieties, Cayenne annatto is the most esteemed, and is considered to be the richest in colouring matter. It should contain from 10 to 12 p.c. of the pure dye, and not more than 5 p.c. of ash, whereas the amount of colouring matter in the Bengal product is frequently lower than 6 p.c.

In 1848 Dumontal devised a new method for the preparation of annatto, in which fermentation is avoided, and the pulp is simply washed out from the capsules and off the seeds. The product known as *bixin* is said to be five to six times more valuable than ordinary annatto (Crookes, Dyeing and Calico-Printing).

The colouring matters of this dyestuff were first investigated by Chevreul (Leçons de chimie appliquée à la Teinture), who isolated two substances, one yellow, which was called *orrelline*, soluble in water, and a second, *bixin*, which is red and very sparingly soluble.

Bixin, the useful colouring matter, was subsequently examined by numerous chemists, who were only successful in preparing it as an amorphous powder, and its isolation in a crystalline condition was first achieved by Etti (Ber. 7, 446 ; 11, 864).

Etti digested 1·5 kilos of purified annatto

ALCOHOLOMETRY.

Indication of Sikes' hydrometer at 15·6°	British proof spirit	American proof spirit at 15·°6	Alcohol by weight (Germany)	Alcohol by volume at 15° (France)	at 15·6° (Tralles)	Russia	Holland	Spain (Cartier)	Switzerland (Beck)
	Overproof								
A.0.	73·5	198·2	98·2	98·9	99·1	—	25·3	43·5	42·6
A.1.	72·9	197·5	97·7	98·6	98·8	—	25	43·2	—
A.2.	72·2	196·8	97·2	98·2	98·4	—	—	—	41·8
A.3.	71·6	196·1	96·6	97·8	98·0	—	24·5	—	—
A.4.	71·0	195·3	96·1	97·5	97·7	—	—	42·2	40·9
A.5.	70·3	194·6	95·5	97·1	97·3	—	24	—	—
A.6.	69·6	193·8	94·9	96·7	96·9	—	—	—	—
A.7.	68·9	193·0	94·3	96·3	96·5	—	23·5	41·2	39·6
A.8.	68·2	192·2	93·7	95·9	96·1	—	—	—	—
A.9.	67·5	191·3	93·1	95·4	95·6	99·2	23	—	—
A.10 = 0	66·7	190·4	92·5	95·0	95·2	98·3	—	40·1	38·3
1	66·0	189·6	91·9	94·7	94·8	—	22·5	—	—
2	65·2	188·7	91·3	94·2	94·3	96·3	—	—	—
3	64·4	187·7	90·7	93·8	93·9	—	22	39·1	37·1
4	63·6	186·8	90·0	93·3	93·4	94·4	—	—	—
5	62·8	185·8	89·4	92·8	92·9	—	21·5	—	—
6	61·9	184·9	88·8	92·3	92·4	92·4	—	38·1	35·8
7	61·1	183·9	88·1	91·8	91·9	—	21	—	—
8	60·2	182·9	87·5	91·3	91·4	90·5	—	—	34·9
9	59·3	181·8	86·8	90·8	90·9	—	20·5	37·2	—
10	58·4	180·8	86·1	90·3	90·4	·5	—	—	34·1
11	57·6	179·9	85·6	89·9	90·0	—	20	—	—
12	56·7	178·9	84·9	89·4	89·5	86·6	—	36·2	—
13	55·7	177·9	84·2		88·9	—	19·5	—	32·9
14	54·8	176·8	83·5	88·3	88·4	84·6	—	—	—
15	53·8	175·7	82·8	87·7	87·8	—	19	35·2	32
16	52·9	174·6	82·1	87·2	87·3	82·6	—	—	—
17	51·9	173·4	81·4	86·6	86·7	—	18·5	—	—
18	50·9	172·3	80·7	80·6	86·1	80·6	—	34·2	30·8
19	49·9	171·1	80·0	85·5	85·6	—	18	—	—
20	48·9	170·0	79·3	84·9	85·0	78·7	—	—	30
21	47·9	168·8	78·6	84·3	84·4	—	17·5	—	—
22	46·8	167·7	77·9	83·8	83·9	76·7	—	33	—
23	45·8	166·5	77·2	83·1	83·2	—	17·0	—	28·8
24	44·7	165·3	76·5	82·5	82·6	74·8	—	—	—
25	43·6	164·0	75·8	81·9	82·0	—	—	32	28
26	42·5	162·7	75·0	81·3	81·4	72·8	16·3	—	—
27	41·4	161·5	74·3	80·6	80·7	—	—	—	—
28	40·3	160·2	73·6	80·0	80·1	70·9	15·9	31·1	26·8
29	39·1	158·9	72·8	79·4	79·5		—	—	—
30	38·0	157·6	72·1	78·7	78·8		15·4	—	26
31	36·9	156·3	71·3	78·1	78·2		—	30·1	—
32	35·7	155·0	70·6	77·4	77·5	67	14·9	—	—
33	34·6	153·7	69·9	76·8	76·9		—	—	24·8
34	33·4	152·4	69·1	76·1	76·2	65	14·5	29·2	—
35	32·2	151·0	68·4	75·4	75·5	—	—	—	24
36	31·0	149·6	67·6	74·7	74·8	63·1	14	—	23·2
37	29·8	148·2	66·8	74·0	74·1	—	—	28·2	—
38	28·5	146·8	66·1	73·3	73·4	61·1	13·5	—	—
39	27·3	145·4	65·3	72·6	72·7	—	—	—	22
40	26·0	144·0	64·5	71·9	72·0	59·2	13·1	—	—
41	24·8	142·6	63·8	71·2	71·3	57·2	—	27	—
42	23·6	141·1	63·0	70·5	70·6	—	—	— ·	20·9
43	22·3	139·7	62·2	69·7	69·8	—	12·4	—	—
44	21·0	138·2	61·4	69·0	69·1	55·3	—	26·1	20·1
45	19·7	136·7	60·6	68·3	68·4	—	11·9	—	—
46	18·3	135·2	59·8	67·5	67·6	53·3	—	—	—
47	17·0	133·7	59·0	66·7	66·8	—	11·5	25·2	—
48	15·6	132·1	58·2	65·9	66·0	51·3	—	—	18·9
49	14·3	130·6	57·4	65·1	65·3	—	11	—	—
50	12·9	129·0	56·6	64·3	64·5	49·4	—	24	17·8
51	11·5	127·4	55·8	63·5	63·7	—	10·5		
52	10·1	125·8	55·0	62·7	62·9	47·4			

F 2

Indication of Sikes' hydrometer at 15·6°	Percentage of					Indications of hydrometer of			
	British proof spirit	American proof spirit at 15·°6	Alcohol by weight (Germany)	Alcohol by volume		Russia	Holland	Spain (Cartier)	Switzerland (Beck)
				at 150° (France)	at 15·6° (Tralles)				
	Overproof								
A.10=53	8·7	124·2	54·2	61·9	62·1	----	10·1	----	17
54	7·3	122·6	53·4	61·1	61·3	45·5	----	23·1	----
55	5·8	120·9	52·5	60·2	60·4	----	----	----	----
56	4·4	119·2	51·7	59·4	59·6	43·5	9·4	----	15·9
57	2·9	117·5	50·9	58·5	58·7	----	----	22·2	----
58	1·4	115·7	50·0	57·7	57·9	41·5	9	----	15·1
	Underproof								
59	0·2	114·0	49·2	56·8	57·0	----	----	----	----
60	1·7	112·2	48·3	55·9	56·1	39·5	--	21·3	----
61	3·3	110·5	47·5	55·0	55·2	----	8·3	----	14
62	4·8	108·7	46·6	54·1	54·3	37·6	----	----	----
63	6·4	106·9	45·8	53·2	53·4	----	7·9	----	13·3
64	8·1	105·0	44·9	52·3	52·5	35·6	----	20·4	----
65	9·7	103·1	44·0	51·3	51·5	--	----	----	----
66	11·4	101·2	43·1	50·4	50·6	33·6	7·2	----	12·2
67	13·1	99·3	42·1	49·4	49·6	----	----	----	----
68	14·9	97·2	41·1	48·4	48·6	31·6	6·8	19	----
69	16·7	95·1	40·2	47·3	47·5	----	----	----	11
70	18·6	93·0	39·2	46·3	46·5	29·7	----	----	----
71	20·5	90·8	38·2	45·2	45·4	----	6·1	18·1	----
72	22·4	88·6	37·2	44·1	44·3	27·7	----	----	9·9
73	24·4	86·4	36·2	43·0	43·2	----	5·7	----	----
74	26·4	84·2	35·2	41·0	42·1	25·7	----	----	----
75	28·5	81·8	34·1	40·7	40·9	----	----	16·9	8·8
76	30·7	79·4	33·0	39·5	39·7	23·7	5·1	----	----
77	32·9	76·9	31·9	38·3	38·5	----	----	----	8·1
78	35·3	74·3	30·7	36·9	37·1	21·8	----	16·1	----
79	37·7	71·4	29·5	35·5	35·7	----	4·4	----	--·
80	40·3	68·5	28·2	34·0	34·2	19·8	----	----	7
81	42·9	65·4	26·9	32·5	32·7	----	4·0	----	----
82	45·7	62·3	25·6	31·0	31·2	17·9	----	15	----
83	48·6	58·9	24·2	29·3	29·5	--	3·6	----	6
84	51·7	55·4	22·7	27·5	27·7	15·9	----	----	----
85	54·8	51·7	21·1	25·6	25·8	--	----	14·1	----
86	58·2	47·9	19·5	23·7	23·9	13·9	3·0	----	4·9
87	61·5	44·1	18·0	21·8	2_·0	----	----	----	----
88	65·0	40·2	16·4	19·9	20·1	11·9	----	13·3	----
89	68·4	36·2	14·7	18·0	18·1	----	2·3	----	3·8
90	71·9	32·2	13·1	16·0	16·1	9·9	----	----	----
91	75·2	28·4	11·5	14·1	14·2	----	1·9	12·4	3·1
92	78·4	24·7	10·0	12·3	12·4	7·9	----	----	--
93	81·4	21·3	8·6	10·6	10·7	----	1·5	----	----
94	84·4	17·9	7·2	8·9	9·0	6	----	11·6	2·1
95	87·3	14·6	5·8	7·2	7·3	----	----	----	----
96	90·0	11·4	4·6	5·6	5·7	4	0·9	----	----
97	92·6	8·4	3·4	4·1	4·2	----	----	10·8	1
98	95·1	5·6	2·2	2·7	2·8	2	----	----	----
99	97·6	2·8	1·1	1·4	1·4	----	----	----	----
100	100·0	0·0	0·0	0·0	0·0	0	0	10·1	0·1

graduated to show percentages of alcohol by weight at 15°—apparent percentages at other temperatures being converted into true percentages by means of tables. Duty is, however, charged on the volume of anhydrous alcohol present in a spirit when measured at 15·6°. This system is therefore analogous to the British, with the exception that the dominant temperature at which British proof-strengths are computed is 10°.

In France Gay - Lussac's original volume alcoholometer and tables have been corrected to the new values for densities of mixtures of alcohol and water determined by the ' Bureau national des poids et mesures ' (1884). The density of anhydrous alcohol at 15°/15° is given as 0·79433 in vacuum, as against 0·7947 assumed by Gay-Lussac, and the difference between the graduations of the old and new official instruments reaches a maximum of 0·4 p.c. for spirits containing from 20 to 21 p.c. of alcohol by volume. Thus 20° at a temperature of 15° on the new legal centesimal alcoholometer indicates spirit containing 20 p.c. by volume of alcohol, and corresponds to 20·4° on Gay-Lussac's original instrument. The French spirit tables indicate, at temperatures extending from

0° to 30°, the percentage by volume of alcohol which a liquid contains at 15°.

Previous to the adoption of Gay-Lussac's alcoholometer and tables by the French Government, Cartier's areometer was used as the Revenue instrument. Its stem is graduated from 10 to 45 in divisions of equal length, and indicates the concentration of a spirituous liquid by arbitrary degrees, which serve as spirit-strengths for charging duty. Cartier's areometer is still used in Spain and South America.

In Switzerland, Beck's hydrometer is used for spirit assaying, and, like Cartier's instrument, of which it is a modification, floats at the lowest indication in distilled water at 12·5° (10°R.).

By means of the table on p. 67 the indications of any one of these instruments at 15·6° can be converted into degrees of any other, and British fiscal strengths compared with those of other countries.

An indispensable step to a correct assay of spirit is the removal of any foreign matter which may be in solution in the alcoholic mixture. In the case of potable spirits, wines, liqueurs, &c., the spirit is freed from saccharine and other dissolved matter by distillation. The distillation of a strong spirituous liquid into its own volume so as to obtain an accurate determination of the amount of alcohol present is impracticable with the apparatus and the methods of distillation commonly used, so that although it is possible to distil without loss spirits of underproof strength into the same volume, it is necessary to dilute overproof spirits and distil into two, three, or four times the original volume. The amount by which the true alcoholic strength of brandy or rum differs from the apparent strength, as indicated by the hydrometer or a density determination, is termed the 'obscuration.'

In the case of medicinal preparations, flavouring essences, &c., which yield distillates containing essential oils and volatile substances, special treatment is necessary before a pyknometrical determination of spirit is possible. In these circumstances the sample or distillate is mixed with water in a separator so that the mixture shall contain not more than 20–25 p.c. by volume of alcohol, and common salt is added in quantity sufficient to saturate the liquid. The mixture is then shaken vigorously with 50–100 c.c. of light petroleum, and after remaining a short time, the aqueous layer is extracted, if necessary, a second time with petroleum (for instance when chloroform or ether is present), and finally drawn off into a flask and distilled. In the case of soap liniments and similar preparations, dilute sulphuric acid is used instead of salt, and the aliphatic acids and volatile matters removed by petroleum before distilling (Chem. Soc. Trans. 1903, 314). Preparations containing iodine are decolourised with sodium thiosulphate, and excess of caustic soda added to prevent decomposition of the tetrathionate during distillation. Similarly, volatile acids must be neutralised, and ammoniacal liquids distilled from dilute sulphuric acid solution.

For the estimation of ethyl alcohol in fusel oil, or liquids containing fusel oil, the salt-petroleum process may be employed, but as the higher alcohols cannot be wholly eliminated by this method, the specific refraction of the distillate is determined by the Zeiss Immersion Refractometer. The refractions of mixtures of ethyl alcohol and water have been determined at various temperatures by Wagner and Schultze (Zeitsch. anal. Chem. 1907, 508) and others, and a near approximation to the true alcoholic content of a fusel oil mixture, treated as above described, can be obtained by applying to the apparent percentage by volume of alcohol, as indicated by the density of the distillate, a subtractive correction of 0·5 p.c. for each degree of difference between the refractometer reading as found at 15·6°, and that required for a mixture of ethyl alcohol and water corresponding to the ascertained density. This method of eliminating foreign matters in spirit assaying, from a knowledge of their influence on the specific refractions of aqueous alcoholic mixtures, is capable of wide application, and has been utilised, for instance, by Leach and Lythgoe (Amer. Chem. J. 1905, 964) for determining the proportion of methylated spirits in a spirituous liquid (v. REFRACTOMETER).   J. H.

ALCORNIN or **ALCORNOL.** An alcohol, $C_{22}H_{54}O$, of the nature of phytosterol found in Alcornoco bark (Hartwich and Dünnenberger, Arch. Pharm. 1900, 341).

ALCOVINOMETER. An instrument for determining the alcoholic content of a wine by observing its ascent in a capillary tube.

ALDEHYDE   *Acetaldehyde* C_2H_4O or $CH_3 \cdot COH$. A product of the oxidation of ordinary (ethylic) alcohol. Aldehyde occurs, together with its polymerides metaldehyde and paraldehyde, in the ' first runnings ' from the stills in the rectification of alcohol which has been filtered through charcoal (Krämer and Pinner, Ber. 2, 403; 4, 787; Johnson, J. Soc. Chem. Ind. 8, 57; Hewitt, *ibid.* 21, 97); the best yield is obtained from the alcohol manufactured from potatoes and from the sugar beet. It is also present in crude wood spirit (Krämer and Grodzki, Ber. 9, 1921); in crude petroleum (Robinson, J. Soc. Chem. Ind. 18, 232); in wine during the process of ageing (Trillat, Compt. rend. 136, 171); and in certain circumstances in the fermentation products of alcohol (Trillat, Compt. rend. 146, 645; Trillat and Souton, 146, 996 ; Kayser and Demolon, 146, 783).

Aldehyde is also formed when calcium formate is heated with calcium acetate (Limpricht, Annalen, 97, 369), and when lactic acid and the lactates are distilled with manganese dioxide and sulphuric acid (Städeler, Annalen. 69, 333); it is also one of the products of the dry distillation of sugar (Völckel, Annalen, 87, 303).

Preparation.—Aldehyde is formed by the oxidation of alcohol by means of platinum black (Döbereiner, Gm. 8, 274), of manganese dioxide and sulphuric acid (Liebig, Annalen, 14, 133), of potassium dichromate and sulphuric acid (Städeler, J. 1859, 329), of metallic catalysers (Bouveault, Bull. Soc. chim. 1908, 3, 117; Sabatier and Senderens, Compt. rend. 136, 738), or when alcohol is passed through an iron tube heated to 710°–750° (Ipateff, Ber. 34, 596).

According to Lang (J. Soc. Chem. Ind. 22, 571), the most useful oxidising agents for converting alcohol to aldehyde are the manganic salts. When prepared by Liebig's method, 2 parts of 80 p.c. alcohol are heated with 3 parts of manganese dioxide, 3 parts of

sulphuric acid, and 2 parts of water, and the distillation carried on until the distillate begins to show an acid reaction; this point is reached when about three parts have collected in the well-cooled receiver. The distillate containing alcohol, acetal and ethereal salts is then distilled with an equal weight of calcium chloride, and $1\frac{1}{2}$ parts collected; this is again rectified with an equal weight of calcium chloride and $\frac{3}{4}$ part distilled over. The product so obtained is nearly anhydrous, but still contains alcohol and small quantities of ethereal salts; to free it from these, it is dissolved in 2 vols. of ether, saturated with ammonia in the cold, and the aldehyde-ammonia which separates is collected, dissolved in water, distilled with dilute sulphuric acid in a water-bath, and the distillate rendered anhydrous by rectification over calcium chloride at as low a temperature as possible.

Improved methods and apparatus for oxidising alcohol into aldehyde are described by Boult (J. Soc. Chem. Ind. 15, 668; Fournier, *ibid.* 16, 695).

Commercially, aldehyde is obtained from the ' first runnings ' of the alcohol stills. A special form of still in which the separation of aldehyde from alcohol is brought about during the rectification of the latter is figured and described by Galland (Dingl. poly. J. 259, 225).

Substituted acetaldehydes applicable to perfumery can be obtained by condensing a ketone with a halogen or amino substituted acetic ester in the presence of sodium. The a-hydroxyacrylic ester thus obtained is saponified and decomposed by heat or distillation under reduced pressure (J. Soc. Chem. Ind. 23, 455).

Properties.—Aldehyde is a colourless liquid b.p. $20\cdot8°$, m.p. $-120\cdot7°$, and sp.gr. $0\cdot80092$ at $0°$ (Kopp, Annalen, 64, 214); $0\cdot79509$ at $10°$, $0\cdot79138$ at $13°$, $0\cdot78761$ at $16°$ (Perkin, Chem. Soc. Trans. 45, 475). It has an extremely pungent suffocating odour; it is very inflammable, and burns with a feebly luminous flame.

It is soluble in all proportions in alcohol, ether, and water, and is separated from the aqueous solution as an ethereal layer on addition of calcium chloride. When heated with aqueous soda, potash, or barium hydroxide, so-called aldehyde resin is obtained as a brown mass (Liebig, *l.c.*; Weidenbusch, Annalen, 66, 153; Lederer, Monatsh. 22, 536). Sodium amalgam converts aldehyde into ethyl alcohol, a small quantity of β-butyleneglycol, which is also formed by the action of magnesium amalgam (Meunier, Compt. rend. 134, 472; Tistschenko and Grigoreeff, J. Russ. Phys. Chem. Soc. 38, 540; Voronkoff, *ibid.* 38, 547), being formed simultaneously (Kekulé, Annalen. 162, 310). With sodium, acetaldehyde reacts violently, producing the compound $CH_2 : CH\cdot ONa$, which rapidly polymerises to a brown substance, whilst if the reaction takes place in presence of benzoic chloride in ethereal solution aldehydoaldolbenzoate $C_{13}H_{16}O_4$, m.p. $86°-87°$, is formed (Freer, Amer. Chem. J. 18, 552; Annalen, 293, 326). Phosphorus pentachloride reacts with it, yielding ethylidene dichloride (Geuther, Annalen, 105, 323).

In presence of reduced nickel hydrogen reduces aldehyde to ethyl alcohol, a good yield and pure product being obtained (Sabatier and Senderens, Compt. rend. 137, 301). With potas-

sium permanganate, acetic acid is formed, but in presence of excess of potash, oxalic and carbonic acids are also formed (Denis, Amer. Chem. J. 38, 561).

When subjected to electrolysis in faintly alkaline or neutral solution it is decomposed into alcohol and acetic acids (Slaboszewicz, Chem. Zentr. 1903, i. 279; Law, Chem. Soc. Trans. 1905, 198; Jackson and Laurie, *ibid.* 1906, 156), whilst when heated alone to high temperatures carbon monoxide and methane are the chief products (Bone and Smith, Chem. Soc. Trans. 1905, 910).

Acetaldehyde and its dimethyl derivative have antiseptic properties (Coblenz, J. Soc. Chem. Ind. 17, 728; Pasqualis, Chem. Zentr. 1897, ii. 10, 12). It is also useful in photographic developing (Seyewetz, Bull. Soc. chim. 19, (3) 134), and the vapour or solution in alcohol or benzene slowly hardens dry gelatine films (Beckmann, Chem. Zentr. 1896, ii. 930).

Aldehyde readily polymerises in the presence of small quantities of various substances, such as sulphuric acid, phosgene, zinc chloride, hydrogen chloride, sulphur dioxide, the halogens, particularly iodine, &c., and two compounds are obtained the relative quantities of which depend upon the temperature; the chief product being *metaldehyde* $(C_2H_4O)_3$ (Hanriot and Oeconomides, Ann. Chem. Phys. [5] 25, 227; McIntosh, Chem. Soc. Trans. 1905, 790; Zecchini, Gazz. chim. ital. 22, ii. 586), when the action takes place in a freezing mixture; and the isomeric *paraldehyde* (elaldehyde) when it occurs at the ordinary temperature (Kekulé and Zincke, Annalen, 162, 125; Desgrez, Bull. Soc. chim. 11, (3) 362; Wachhausen, Chem. Zentr. 1897, i. 493; Ciamician and Silber, Ber. 35, 1080).

Paraldehyde is a colourless liquid, crystallising below $10°$ in large transparent prisms; b.p. $124°$ at $759\cdot8$ mm. and sp.gr. $0\cdot998$ at $15°$ (Kekulé and Zincke); sp.gr. $0\cdot99925$ at $15°$ (Perkin, Chem. Soc. Trans. 45, 479); b.p. $123\cdot2°-123\cdot5°$ at 744 mm. (Brühl, Annalen, 203, 26). When condensed with hydroxyquinol, it produces yellow dyes (Liebermann and Lendenbaum, Ber. 37, 1171, 2728).

Metaldehyde crystallises in needles or tetragonal prisms, sublimes without previous fusion at $112°-115°$, and when heated in sealed tubes at $120°$ is entirely reconverted into ordinary aldehyde (Friedel, Bull. Soc. chim. 9, (3) 384). According to Troeger (Ber. 25, 3316), after standing for ten years a sample was converted into aldehyde and paraldehyde, but according to Hantzsch and Oechslin (Ber. 40, 4341), metacetaldehyde is not isomeric with paracetaldehyde, and is quite stable when pure. Orndorff and White (Amer. Chem. J. 16, 43) state that when it is allowed to stand for some time the metaldehyde is converted into tetraldehyde $(C_2H_4O)_4$.

Neither polymeride is resinised by aqueous soda or potash, but in other reactions they behave generally as ordinary aldehyde and yield similar products (Kekulé and Zincke).

Reactions.—Aldehyde in aqueous solution very readily reduces an ammoniacal solution of silver nitrate giving a bright metallic mirror. Acetaldehyde (and all aldehydes which are stable in aqueous soda solution) can be detected by adding to a solution of the suspected

substance in dilute alkali a fresh solution of 1 part of paradiazobenzenesulphonic acid in 60 parts of water rendered alkaline with a little soda, and then some sodium amalgam; if an aldehyde is present, a reddish-brown colour is developed after the mixture has stood for 10–20 minutes (Penzoldt and Fischer, Ber. 16, 657).

A solution of rosaniline decolourised by sulphurous acid (Villiers and Foyolle, Compt. rend. 119, 75), or magenta bleached by sunlight (Bieser, Chem. Zentr. 1899, ii. 848), regains its original colour on addition of an aldehyde. This reaction is due to the formation of coloured compounds by the condensation of the aldehyde and magenta (Urbain, Bull. Soc. chim. 1896, iii. 15, 455). With salts of m-diamines aldehydes give coloured solutions with intense greenish fluorescence (Bitto, Frdl. 36, 369). With sodium nitroprusside and alkali acetaldehyde gives a cherry-red colouration, whilst if trimethylamine is first added a blue colour is produced (Bitto, Annalen, 267, 372; 269, 377; Denigès, Bull. Soc. chim. 17, (3) 381; Simon, Compt. rend. 125, 1105; Bull. Soc. chim. 19, (3) 297). Thiosemicarbazide mixed with an aldehyde in acetic, alcoholic, or aqueous solution yields characteristic thiosemicarbazones. Acetaldehydethiosemicarbazone has m.p.146°(Freund and Schander, Ber. 35, 2602).

Other tests for aldehydes are described by (Ihl, Chem. Zeit. 14, 1571; Doebner, Ber. 27, 352, 2020; Lumière and Seyewetz, Bull. Soc. chim. 19, (3) 134; Rimini, Atti Real. Acad. Lincei, 1901, 10, 355; Murco, Compt. rend. 31, 943; Riegler Frdl. 42, 168; Behrens, Chem. Zeit. 26, 1125; Sadtler, J. Soc. Chem. Ind. 23, 387; Prud'homme, Bl. Soc. Ind. Mulhouse, 1904, 74, 169; Leys, J. Pharm. Chim. 1905, 22, 107; Auld and Hantzsch, Ber. 38, 2677.

Aldehyde readily yields condensation compounds; thus when allowed to remain in the cold with dilute hydrochloric acid, or with aqueous solutions of zinc chloride or of salts having an alkaline reaction, such as potassium carbonate, aldol is obtained, whilst croton-aldehyde is formed when it is heated with concentrated hydrochloric acid (Kekulé, Annalen, 162, 92; Kling and Roy, Compt. rend. 144, 1111).

Aldehyde has also been condensed with other aldehydes and ketones (Wallach, Chem. Zentr. 899, ii. 1024; Schmalzhoffer, Monatsh. 211, 671; Wogrinz, ibid. 22, 1; Weiss, ibid. 25, 1065; Schachner, ibid. 26, 65; Salkind, J. Russ. Phys. Chem. Soc. 37, 484; Rainer, Monatsh. 25, 1035; Ehrenfreund, ibid. 26, 1003); with amines (Eibner and Peltzer, Ber. 33, 3460; Eibner, Annalen, 328, 121; Knoevenagel, Ber. 37, 4461); with rhodanic and substituted rhodanic acids forming stable dyeing compounds (Andreasch and Zipser, Monatsh. 24, 499; 26, 1191; Zipser, ibid. 23, 592; Stachetz, ibid. 26, 1209; Bergellini, Atti Real. Acad. Lincei, 15, 35, 181; Andreasch, Monatsh. 27, 1211; 29, 399; Wagner, ibid. 27, 1233); with methyl ketole forming leuco- bases of the dyes of rosaniline type (Freund and Lebach, Ber. 36, 308; Freund, Ber. 37, 322); with indole dyes, also forming leuco- bases (Loew, Ber. 36, 4326); with cyanides and cyanacetic esters (Claisen, Ber. 25, 3164; Barbier and Bouveault, Compt. rend. 120, 1269; Kohn, Monatsh. 19, 519; Wade, Chem. Soc. Proc. 1900, 156; Bertini,

Gazz. chim. ital. 31, i. 265; Fiquet, Bull. Soc. chim. 7, (3) 767); with phenyl hydrazones (Fischer, Ber. 29, 793; 30, 1240; Pechman, Ber. 31, 2123; Bamberger and Pemsel, Ber. 36, 85; Lockmann and Liesche. Annalen, 342, 14; Medvedeff, Ber. 38, 1646, 2283; Maurenbrecher, Ber. 39, 3583). Substances capable of use in perfumery can be obtained by condensing aldehydes with negatively mono- substituted acetic acids in presence of ammonia or a primary or secondary amine (J. Soc. Chem. Ind. 24, 689, 1323). (For compounds of other substances with aldehydes, see Hooker and Carnell, Chem. Soc. Proc. 1893, Fischer, Ber. 27, 165; Claisen, Annalen, 237, 261; Conncler, Chem. Zeit. 20, 585; Kietreiber, Monatsh. 19, 735; Bamberger and Müller, Ber. 27, 147; Rassow, J. pr. Chem. 172, 136, 129; Betti, Gazz. chim. ital. 30, ii. 310; 33, i. 27; Koenigs, Ber. 34, 4336; Moureu and Desmots, Compt. rend. 134, 355; Knoevenagel, Ber. 36, 2136; Hann and Lapworth, Chem. Soc. Trans. 1904, 46; Simon and Conduché, Compt. rend. 138, 977; Darzens, Compt. rend. 142, 214; Eissler and Pollock, Monatsh. 27, 1129; Rolla, Gazz. chim. ital. 37, 623; Senier and Austin, Chem. Soc. Trans. 1907, 1233; Wohl, Ber. 40, 4679; Braun, Ber. 41, 2169; Zeisel and Bitto, Monatsh. 29, 591.)

Additive compounds.—Aldehyde not only shows a strong tendency to yield polymerides and condensation compounds, but unites directly with a large number of substances.

(1) Compounds with alcohols (v. ACETAL).

(2) Compounds with acids :—Geuther, Annalen, 106, 249; Lieben, ibid. 106, 336; 178, 43; Rübencamp, ibid. 225, 279; Schiff, Ber. 9, 304; Ponzio, J. pr. Chem. 161, 431; Schroeter, Ber. 31, 2189; Annalen, 303, 114; Delépine, Compt. rend. 133, 876; McIntosh, Amer. Chem. J. 28, 588.

(3) Compounds with alkaline sulphites :— Aldehyde forms definite crystalline compounds when dissolved in concentrated aqueous solutions of the acid sulphites (bisulphites) of the alkali metals. The *potassium* salt $C_2H_4O,KHSO_3$ crystallises in indistinct needles; the *sodium* salt $C_3H_4O,NaHSO_3+\frac{1}{2}H_2O$, in fine needles or nacreous plates. The ammonium compound has the formula $C_2H_4(OH)SO_2 \cdot NH_2$. These salts are almost insoluble in excess of the sulphite, and separate in the crystalline state; from them aldehyde can be obtained by distillation with a stronger acid, an alkaline carbonate, or by alkali nitrites (Bunte, Annalen, 170, 305; Freundler and Bunel, Compt. rend. 132, 1338; Seyewetz and Burdin, Compt. rend. 141, 259; Rosenheim, Ber. 38, 2005; Coppock, Chem. News, 1907, 225). With hyposulphites in neutral or acid solutions aldehyde hyposulphites are obtained; $2RCHO,M_2S_2O_4$ (J. Soc. Chem. Ind. 25, 475); by varying the condition sulphoxylates of type $RCH_2 \cdot SO_3M$ can be formed (D. R. P. 180529). Crystalline thioaldehydes are obtained by the action of hydrogen sulphide on an acidified alcoholic solution of aldehyde (Baumann and Fromm, Ber. 22, 2600; Ber. 24, 1419, 1457; Klinger, Ber. 32, 2194; Drugman and Stockings, Chem. Soc. Proc. 1904, 116; Vanino, J. pr. Chem. 185, 367).

(4) Compound with ammonia :—*Aldehyde-ammonia* $C_2H_4O \cdot NH_3$, obtained by leading dry ammonia into aldehyde in ethereal solution

(Liebig, Annalen, 14, 144; Jean, Bull. Soc. chim. 13, (3) 474; Trillat, *ibid.* 13, (3) 689; Delépine, Compt. rend. 125, 951; 128, 105; 137, 984; 144, 853; Coninck, Compt. rend. 126, 1042; Tschitschibabin, J. Russ. Phys. Chem. Soc. 37, 1229; Duden, Bock and Reid, Ber. 38, 2036; Ciamician and Silber, Ber. 38, 1671; 39, 3942), crystallises in large rhombohedra, melts at 70°–80°, boils at 100° without decomposition, and is decomposed into its constituents on distillation with dilute acids. When hydrogen sulphide is passed through a mixture of aldehyde ammonia and ether a crystalline substance SH·CHMe·NH·CHMeOH, m.p. 60°–63°, is obtained (Chabrié, C. R. Soc. Biol. 1896, 3, 72).

(5) Compounds with hydrocyanic acid :—(Tiemann, Ber. 14, 1965; Strecker, Annalen, 91, 349; Erlenmeyer and Passavant, *ibid.* 200, 120).

(6) Compounds with metallic salts :—With mercuric sulphate it forms the compound SO_4: $(HgO)_2 : HgC_2H_4O$ (Denigès, Compt. rend. 128, 429); with mercuric nitrate, $C_2Hg_2NO_4H$ (Hofmann, Ber. 31, 2212); and with mercuric acetate alkaline solution at 0°, CMe·HOHgO (Lasserre, J. Pharm. 1905, 22, 246). With gold chloride it forms a coloured colloidal solution (Garbowski, Ber. 36, 1215); and with magnesium bromide, the compound $MgBr_2,3CH_3CHO$ (Menschutkin, Zeitsch. anorg. Chem. 53, 26).

Substitution-derivatives. — The action of chlorine on aldehyde has been studied by Wurtz (Annalen, 102, 93), Wurtz and Voigt (Bull. Soc. chim. 17, 402), and by Pinner (Annalen, 179, 21; Coblenz, *l.c.*; Freundler, Bull. Soc. chim. 1, (4) 66; Freundler, Compt. rend. 143, 682). Pinner finds that when chlorine is passed into ordinary aldehyde at 10°, metaldehyde and paraldehyde are first formed, and these subsequently yield substitution-derivatives, of which chloral is the chief product. Butyric chloral and dichloraldehyde being formed in smaller quantity. The following derivatives have been prepared :—*Chloraldehyde* $CH_2Cl·CHO + \frac{1}{2}H_2O$ (Natterer, Monatsh. 3, 446); *dichloraldehyde,* $CHCl_2·CHO$ (Grimaux and Adams, Bull. Soc. chim. 34, 29; Wohl and Roth, Ber. 40, 212); *trichloraldehyde (v.* CHLORAL).

The bromine derivatives, and the action of bromine on aldehyde, have been examined by Pinner (Ber. 7, 1499, and *l.c.*; Bugarsky, Zeitsch. physikal. Chem. 48, 63; Freundler, Compt. rend. 140, 1693; Mauguin, Compt. rend. 147, 747).

Aldehyde blue is obtained by treating pararosaniline with aldehyde or, better, paraldehyde in aqueous acid solution, and precipitating the dye with sodium chloride. It is soluble in alcohol and ether, and when treated with strong hydrochloric acid is converted into a reddish yellow base which shows all the properties of a rosaniline dye (Gattermann and Wichmann, Ber. 22, 227). By slightly varying the conditions in the preparation of aldehyde blue, *aldehyde green* can also be obtained (Miller and Plüchl, Ber. 24, 1700).

ALDEHYDES. The name aldehyde originally assigned to the compound obtained by the limited oxidation of ethyl alcohol, has come to possess a wider signification, and is now used as a generic term for a class of organic substances which are similarly derived from the primary alcohols. In composition the aldehydes differ from the alcohols from which they are derived by containing two atoms of hydrogen fewer in the molecule; whilst in their chemical behaviour they all exhibit the general properties of the typical member of the series, acetaldehyde.

There are general methods for preparing aldehydes: (1) By the action of organomagnesium compounds on the esters of orthoformic ester thus :

$$HC(OR)_3 + R'MgI = ROMgI + R'HC(OR)_2$$
$$R'HC(OR)_2 + H_2O = R'HCO + 2R·OH$$
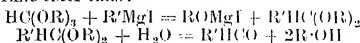
(Tschitschibabin, Ber. 37, 186; Gattermann and Maffezzoli, Ber. 36, 4152; Williams, Chem. Soc. Proc. 1906, 22). (2) By decomposing with water the products of reaction between di-substituted amino-formaldehydes on alkyl, aryl, or hydroxyl magnesium halides (J. Soc. Chem. Ind. 23, 1237; Bouveault, Bull. Soc. chim. 31, (3) 1306, 1322). (3) By the action of organo-magnesium compounds on formic acid or alkyl formates (J. Soc. Chem. Ind. 24, 690; Chem. Zentr. 29, 667; D. R. P. 157573).

Other methods are described by Stoermer (Ber. 39, 2288); Blaise (Compt. rend. 138, 697); Faworsky (J. Russ. Phys. Chem. Soc. 38, 741); Tiffeneau (Compt. rend. 37, 1260); Behal and Sommelet (D. R. P. 177614, Compt. rend. 138, 89); Guerbet (Compt. rend. 146, 132); Mossler (Monatsh. 29, 69); Merling (Ber. 41, 2064, 2217) Aliphatic dialdehydes have been prepared by Wohl and Schweitzer (Ber. 39, 890); Sinais (Bl. Ind. Mulhouse, 1907, 75).

ALDEHYDE GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

ALDEHYDINE *v.* BONE OIL.

ALDEHYDINES. Compounds formed by the condensation of ortho-diamines with aldehydes (Ladenburg, Ber. 10, 1126) (*v.* AMINES).

ALDER BARK. (*Aune,* Fr.; *Erle,* Ger.) *Alnus glutinosa* (Gaert.). Used for tanning and dyeing. The percentage of tannin varies from 16 to 18 (Eitner, Zeit. f. d. Chem. Grossgew. 3, 668; 4, 279).

The tannin appears to be a methyl tannin like that of the oak; it gives a reddish-blue precipitate with ferrous acetate, an olive-green precipitate with ferrous sulphate, and is precipitated by a gum solution.

A solution of the bark is employed for obtaining black, greys, and browns on linen; in Germany for reds; and in Kamchatka for colouring skins a red tint.

ALE *v.* BREWING.

ALEMBROTH, SALT OF. A compound of mercuric chloride and sal ammoniac

$$2NH_4Cl,HgCl_2,H_2O$$
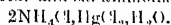
formed by mixing the two salts in suitable proportions. Also called by the alchemists Salt of Wisdom.

ALEURITES CORDATA (Steud.). The seeds of this euphorbiaceous plant, which is found largely in Japan, yield Japanese wood-oil (*q.v.*).

ALEURONE GRAINS. Organised granules deposited in the cells of many seeds of plants, generally near the exterior, in which the proteins are mainly concentrated. They were so named by Hartig, who first described them. In many plants, the aleurone grains possess the shape of

crystals. Botanists, indeed, regard them as consisting of two parts : (1) a *crystalloid*, crystal-like protein body, and (2) one or more rounded *globoids* mainly composed of mineral matter, in which phosphoric acid, lime, and magnesia are usually the largest constituents.

When the aleurone grains exhibit the form of crystals, it is generally found that they are soft and swell up if treated with weak acids or alkalis. The term 'crystalloid,' as used by botanists in this connection, has reference to the appearance of the aleurone grains, and not to their property of diffusion when dissolved through membranes. According to Tschirch and Kritzler (Chem. Zentr. 1900, ii. 585), the aleurone grains of a variety of plants consist mainly of globulins. The crystalloids consist of at least two globulins, which are soluble in dilute, but insoluble in concentrated saline solutions (*e.g.* ammonium sulphate, sodium chloride with trace of acetic acid, potassium dihydrogen phosphate).

A small amount of an albumose is also probably present. The globoids contain a globulin and mineral matter, especially calcium, magnesium, and phosphoric acid ; they are soluble in concentrated solutions of ammonium sulphate, acidified sodium chloride, or potassium dihydrogen phosphate. The grains with their enclosures are reserve-food materials which are consumed when the seed germinates. They originate as liquid ' vacuoles,' in which an increasing amount of protein material is gradually deposited. The germinating power of seeds probably depends upon the solubility of the crystalloids in dilute sodium chloride solution.

According to Posternak (Compt. rend. 1905, 140, 322), aleurone grains often contain anhydro-oxymethylene diphosphoric acid (phytine). He found the following amounts of nitrogen and mineral substances in the aleurone grains of (1) spruce fir, (2) sunflower, (3) hemp, (4) white lupin :—

	N	K	Ca	Mg	Fe	Mn	P	S	Si
1.	12·97	2·50	0·37	1·25	0·09	0·25	2·67	0·64	0·35
2.	10·22	2·20	0·33	1·46	0·05	trace	2·78	0·64	0·24
3.	12·88	2·71	0·27	1·67	0·05	trace	3·83	0·81	0·36
4.	10·70	—	0·11	0·28	—	0·11	0·61	—	0·01

Sodium and chlorine were not found.   H. I.

ALFA *v.* HALFA.

ALFALFA. The Spanish name for lucerne, *Medicago sativa* (Linn.).

ALGÆ. (*Varech* or *Algues*, Fr. ; *Algen*, Ger.) A class of cryptogamous plants including the green, brown, and red seaweeds and vegetable plankton growing in sea-water, and allied mainly green fresh-water plants, including diatoms, desmids, and 'conferva'-like forms. Many of the salt-water species are edible; none of them is poisonous.

Rhodymenia palmata (Linn.) (dulse, dylish, or dellish) and *Alaria esculenta* (murlins) are used as food by the peasantry of the Highlands and of Ireland. *Porphyra laciniata* (Lightf.) (laciniated purple laver), very abundant in the British coasts, is sold in England as laver, in Ireland as sloke, and in Scotland as slaak. *Chondrus crispus* (Linn.) (carrageen, Irish or pearl moss) is collected on the west coast of Ireland, and is frequently used there by painters and plasterers as a substitute for size. It is also used in making jellies, &c., in medicine ; and a thick mucilage scented with some prepared spirit is sold as ' bandolin,' ' fixature,' or ' elysphitique,' and is employed for stiffening silks.

Amongst other algæ having an economic value are Ceylon moss or edible moss (*Gracilaria lichenoides*), found in the Indian archipelago ; the agar-agar of Malacca, or agal-agal of China, which is derived from *Gracilaria lichenoides*, *Eucheuma spinosum* (Linn.) and other algae (*see* AGAR). The substance is now much used in bacteriological research as a nutrient jelly ; for gumming silks, paper, &c., and for making a paste not liable to be eaten by insects.

Manna, or mannite, can be obtained from *Laminaria saccharina* (Lamx.) or sugar wrack, found on sandy shores, attached to pebbles.

The following table shows the composition of various species of algæ ; the quantity of nitrogen in some of them is remarkably large :—

Alga	Water	Dry matter	Per cent. nitrogen in dry matter	Protein contained in dry matter
Chondrus crispus, bleached from Bewlay Evans	17·92	82·08	1·534	9·587
Chondrus crispus, bleached second experiment	19·79	80·21	1·485	9·281
Chondrus crispus, unbleached Ballycastle	21·47	78·53	2·142	12·387
Chondrus crispus, unbleached, second experiment	19·96	80·04	2·510	15·687
Gigartina mamillosa, Ballycastle	21·55	78·45	2·198	13·737
Laminaria digitata, or dulse tangle	21·38	78·62	1·588	9·925
	16·56	83·44	3·465	21·656
Porphyra laciniata	17·41	82·59	4·650	29·062
(*Sarcophyllis*) *edulis*	19·61	80·39	3·088	19·300
Alaria esculenta	17·91	80·09	2·424	15·150

In addition to the large amount of chlorine in marine algæ (up to 38 p.c. of the ash) there are often not inconsiderable quantities of iodine, the presence of which is responsible for the employment of seaweeds in the composition of certain ' anti-fat ' specifics.

Certain algæ are characteristic of water containing sewage and putrefactive substances in quantity, and some algæ play an important *rôle* in the disinfection of polluted rivers.

ALGAROBILLA. Algarobilla consists of the pods of *Cæsalpina brevifolia*. The tannin, which appears to be a mixture of allagetannin and gallotannin, lies in semi-resinous particles

adhering loosely to the somewhat open frame-work of the fibre. It is one of the strongest tannin matters known, and contains on the average 45 p.c. In character it resembles divi-divi, and its extract is somewhat prone to fermentation. It is very suitable for tanning and also for dyeing purposes.

ALGAROTH, POWDER OF. *Pulvis Alga-rothi, English Powder.* A crystalline oxy-chloride of antimony, obtained by pouring anti-mony chloride into hot water. Used in the preparation of tartar emetic (*v.* ANTIMONY).

ALGIN. A nitrogenous body obtained from seaweed, somewhat resembling albumen (*v.* IODINE).

ALGODONITE. A copper arsenide of a steel-grey colour. Found in the Lake Superior copper-mining district.

ALHAGI CAMELORUM (Fischer), **JAWÁSA, or JAWANI.** A leguminous thorny shrub, widely spread from Greece to dry parts of India, where a drug extracted from it is used for rheumatism, and also as a laxative and diuretic (Pharm. J. [3] 9, 145).

ALIZARIN AND ALLIED COLOURING MATTERS. Madder, *Rubia tinctoria,* which was for a long time used on a large scale in the 'Turkey-red' industry, contains two colouring matters, alizarin and purpurin, of which the former is by far the more important.

Alizarin is not found ready-formed in the madder-root, but exists there as a glucoside called 'ruberythric acid,' which when allowed to ferment, or when boiled with dilute acid, splits up readily into alizarin and glucose.

The colouring matter itself was first isolated from the madder-root in 1827 by Colin and Robiquet, who obtained it by extracting ground madder with hot water and subliming the puri-fied extract carefully in a glass tube.

This method of sublimation was not con-sidered sufficient proof of the existence of alizarin in madder, and it was not till Schunck suc-ceeded in isolating this substance by chemical means from the madder extracts used by dyers that this important point was definitely settled.

In assigning the correct formula to alizarin, considerable difference of opinion existed at first, owing no doubt to some extent to the difficulty experienced in obtaining alizarin in a condition pure enough for accurate analysis.

Schunck proposed the formula $C_{14}H_{10}O_4$, whilst Strecker believed it to be $C_{10}H_6O_3$ and related to 'chloroxynaphthalic acid' (chloro-hydroxynaphthaquinone), a derivative of naph-thalene, since both these substances on oxidation yield phthalic acid.

Strecker's formula was the more generally accepted by chemists, and chloroxynaphthalic acid was looked upon as being simply chlorinated alizarin, the two bodies being thus related :

$C_{10}H_6O_3$
Alizarin.

$C_{10}H_5ClO_3$
Chlorinated alizarin or
Chloroxynaphthalic acid.

In order to prove the relation supposed to exist between these two substances, it was only necessary to replace the chlorine atom in chloroxynaphthalic acid by hydrogen, when alizarin should result.

This operation was eventually accomplished

by Martius and Griess, who obtained thus a substance of the formula $C_{10}H_6O_3$, which was, however, not identical with alizarin, and was therefore supposed to be isomeric with it.

Some time after these experiments of Martius and Griess, Graebe commenced his research on quinones, the working out of which led not only to results which proved beyond a doubt what the chemical nature of alizarin really was, but also eventually resulted in the artificial production of this important colouring matter. In pursuing this investigation Graebe succeeded in preparing chloranil $C_6Cl_4O_2$, by treating phenol with potas-sium chlorate and hydrochloric acid, and in acting on this with caustic potash he found that two of the atoms of chlorine in this compound became replaced by (OK), producing the potash salt of chloranilic acid $C_6Cl_2(OK)_2O_2$, a change the knowledge of which proved to be of the utmost importance in his subsequent experiments on the artificial production of alizarin.

Chloroxynaphthalic acid was now considered by Graebe to be related to naphthalin in much the same way as chloranil was to benzene, *i.e.* to be a derivative of naphthaquinone.

Soon after this the attention of Graebe and Liebermann was turned to alizarin, which they also thought might belong to the quinone series.

In determining the constitution of this substance, the first step was to obtain some information as to the nature of the hydro-carbon from which alizarin was derived, and this was done in the following way : Alizarin prepared from madder was mixed with zinc-dust and heated strongly in a furnace, according to Baeyer's method of reducing benzenoid com-pounds, and in this way a crystalline hydrocarbon was obtained having the composition $C_{14}H_{10}$, which on examination was found to be identical with anthracene, a hydrocarbon previously ob-tained by Dumas and Laurent from coal tar. Using the information already obtained in the research on quinone, Graebe and Liebermann now assumed that alizarin must be a dihydroxy-quinone of anthracene, the relation of these substances to one another being seen from the following formulæ :—

$C_{14}H_{10}$
Anthracene.

$C_{14}H_8O_2$
Anthraquinone.
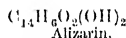
$C_{14}H_6O_2(OH)_2$
Alizarin.

Having thus obtained anthracene from ali-zarin, it was now only necessary to reverse the operation and convert anthracene into alizarin, and the problem of the artificial production of a vegetable colouring matter would be solved for the first time.

In 1862 Anderson, while investigating anthra-cene, obtained from it by oxidation a substance of the formula $C_{14}H_8O_2$, which he named ox-anthracene.

In this substance Graebe and Liebermann recognised the quinone of anthracene (anthra-quinone), the first step in the synthesis of alizarin from anthracene, and in order to convert this quinone into alizarin all that was necessary was to replace two atoms of hydrogen in it by hydroxyl, an operation which is easily done in the following way :-

Anthraquinone when heated with two mole-cules of bromine in sealed tubes is converted into dibromanthraquinone, thus :

$$C_{14}H_8O_2 + 2Br_2 = C_{14}H_6Br_2O_2 + 2HBr.$$
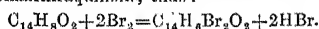
This substance when heated with potash exchanges each of its bromine atoms for (OK), yielding the potash salt of alizarin, $C_{14}H_6(OK)_2O_2$, a reaction which is precisely similar to the formation of chloranilate of potash from chloranil as described above. The potassium alizarate thus obtained, when decomposed with hydrochloric acid, yielded alizarin, and thus the problem of the artificial production of alizarin was solved.

In considering this synthesis, perhaps the most remarkable fact, from a chemical point of view, is that, in consideration of the number of possible isomers of alizarin, just that dibromanthraquinone prepared by Graebe and Liebermann should on treatment with potash have yielded alizarin. Had this not been so, the artificial production of alizarin would no doubt have been very much delayed.

The great importance of alizarin as a dyeing agent induced Graebe and Liebermann to patent this process, which proved, however, to be of no commercial value, owing to the great expense attending the use of bromine, and it was therefore desirable to find some new method which would render their discovery important from a manufacturing point of view.

This was first achieved by W. H. Perkin [1] in the following way:—Sulphuric acid, as is well known, forms with many organic bodies compounds called sulphonic acids, which in composition simply correspond to the substance acted on *plus* sulphuric anhydride.

Thus benzene C_6H_6 when treated with sulphuric acid yields benzenesulphonic acid $C_6H_5SO_3H$; naphthalene $C_{10}H_8$, naphthalenesulphonic acid $C_{10}H_7SO_3H$. When fused with caustic potash these sulphonic acids are split up into the potassium salt of the corresponding phenol and potassium sulphite, thus :

$$C_6H_5SO_3H + 3KOH = C_6H_5OK + K_2SO_3 + 2H_2O.$$

Similarly disulphonic acids when fused with potash are converted into dihydric phenols, thus :

$$C_6H_4(SO_3H)_2 + 6KOH = C_6H_4\frac{OK}{OK} + K_2SO_3 + 4H_2O.$$
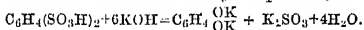
In this second example it will be seen that a body is formed which bears the same relation to benzene as alizarin does to anthraquinone, and it was therefore probable that if anthraquinone were subjected to a similar series of reactions, alizarin would result.

The great obstacle to carrying out this synthesis, in the first instance, was the remarkable stability of anthraquinone in general and particularly towards sulphuric acid, which is so great that it dissolves in moderately hot sulphuric acid without change, and crystallises out again in needles on cooling.

When, however, a mixture of anthraquinone and sulphuric acid was heated very strongly, combination did eventually take place, the product becoming perfectly soluble in water, the solution now containing mono- and disulphonic acids of anthraquinone.

After removing the excess of sulphuric acid from the new product, it was mixed with caustic potash, and heated to about 180°.

During the heating the melt became darker and darker in colour, and eventually almost

[1] It should be mentioned here that while these experiments were in progress, Caro, Graebe and Liebermann were investigating the same reaction in Germany.

black, and on dissolving this in water a rich purple solution was obtained which when acidified with dilute sulphuric acid gave a copious precipitate of alizarin.

The great obstacle to the preparation of alizarin—viz. the use of bromine—was thus removed, and, as the future has proved, a process had been obtained by which this colouring matter could be manufactured in quantity and at a price so cheap as entirely to supersede the old method of dyeing with the madder root.

Another process for the manufacture of artificial alizarin shortly afterwards discovered by W. H. Perkin, and largely used by him on a manufacturing scale, is the following :—

Anthracene is treated with chlorine and thus converted into a beautifully crystalline compound called dichloranthracene $C_{14}H_8Cl_2$.

This substance combines with Nordhausen sulphuric acid, forming a bright-green solution, which contains a sulphonic acid of dichloranthracene. When heated with sulphuric acid this substance undergoes a remarkable change, hydrochloric acid and sulphurous acid are evolved, and a disulphonic acid of anthraquinone formed, thus :

$$C_{14}H_6Cl_2(SO_3H)_2 + H_2SO_4$$
Dichloranthracene-disulphonic acid.
$$= C_{14}H_6O_2(SO_3H)_2 + 2HCl + SO_2.$$
Anthraquinone disulphonic acid.
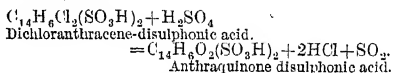
This anthraquinone disulphonic acid when fused with potash yields alizarin.

Alizarin and the other colouring matters of this class will not dye unprepared fabrics ; these must first of all be mordanted.

The mordants used in this case consist of metallic hydroxides—*e.g.* of aluminium, iron, and chromium. Chloride of tin (tin crystals) is also extensively employed.

With alumina mordants alizarin produces shades of red and pink ; with iron mordants, shades of black and purple ; with chromium mordants, a dull purple ; and with tin crystals a bright yellowish orange. These mordants may also be mixed and thus a large variety of different shades produced. A description of the method of application of these various mordants and the processes employed in dyeing with alizarin will be found in the article DYEING.

Since the first production of artificial alizarin on the large scale, the study of this substance and of the various colouring matters related to it has received a large amount of attention at the hands of chemists, the result being that a considerable number of derivatives of anthraquinone have been prepared and examined.

Most of these are either colouring matters themselves, or easily converted into such, several of them being obtained on the large scale in the manufacture of alizarin.

These derivatives may be divided under the following heads :—

(1) Sulphonic acids of anthraquinone.
(2) Monohydroxyanthraquinones.
(3) Dihydroxyanthraquinones.
(4) Trihydroxyanthraquinones.
(5) Higher hydroxylated anthraquinones.

In this article are also included the two dyeing matters, Galleïn and Cœruleïn, which although not actually anthracene derivatives, are very closely allied to them.

Sulphonic acids of anthraquinone.

Anthraquinone α-sulphonic acid

$$C_6H_4\!<^{CO}_{CO}\!>C_6H_3{\cdot}SO_3H. \ (1)$$
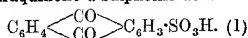
It is a remarkable instance of the influence of a catalyst that whilst anthraquinone ordinarily sulphonates in the 2- position, yet in the presence of quite small amounts of mercury the 1- position is exclusively attacked.

In preparing anthraquinone α-sulphonic acid, 100 pts. of anthraquinone are heated for three hours at 130° with 110 pts. of sulphuric acid containing 29 p.c. sulphuric anhydride, and 0·5 part of mercury.

The free acid is easily soluble in alcohol and water, its lead, barium, and strontium salts are very insoluble in hot water. The calcium salt is fairly soluble, but crystallises on heating the solution. The potassium salt occurs in glistening yellow leaflets.

The further sulphonation of the α acid in presence of mercury leads to the formation of 1 : 5- anthraquinone disulphonic acid, mixed with 1 : 8- and 1 : 7- acids. The same mixture is produced by the direct sulphonation of anthraquinone (100 parts) with 200 parts of sulphuric acid containing 40 p.c. sulphur trioxide, in the presence of mercury (1 part) at 160° for one hour. The mixture of acids is converted into calcium salt and fractionally crystallised. The calcium salt of the 1 : 8- acid is least soluble, the middle fraction is the largest and consists of 1 : 5- whilst the calcium salt of 1 : 7- is easily soluble.

Similarly it has been found that anthraquinone β-sulphonic acid (see below) is changed by sulphuric acid in presence of mercury to a mixture of 2 : 8- and 2 : 5- anthraquinone disulphonic acids (N.B. 2 : 8- is same as 1 : 7). It is strange that the direct sulphonation of anthraquinone in the presence of mercuric sulphate also yields the 2 : 8- disulphonic acid. The constitution of these sulphonic acids has been demonstrated by their conversion into the corresponding hydroxyanthraquinones by heating under pressure with milk of lime.

Literature.—Iljinsky (Ber. 36, 4194–4200) ; Schmidt (Ber. 37, 66–72).

Anthraquinone- 2 or β-sulphonic acid

$$C_6H_4\!<^{CO}_{CO}\!>C_6H_3(SO_3H).$$
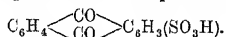
This acid is formed together with a certain amount of anthraquinone disulphonic acid by heating anthraquinone with fuming sulphuric acid to 170° or with ordinary sulphuric acid to 250°–260°.

In preparing it a mixture of one part of fuming sulphuric acid (containing 40–50 p.c. anhydride) and 1–1¼ parts of anthraquinone is gradually heated to about 170° and kept at this temperature for eight or ten hours, the whole being well stirred during the operation.

The product thus formed consists chiefly of the monosulphonic acid together with a little disulphonic acid and unchanged anthraquinone. On diluting with water the anthraquinone separates out, and can easily be filtered off, leaving the sulphonic acids in solution. In order to separate the mono- from the disulphonic acid the clear filtrate is neutralised with carbonate of

soda (or caustic soda). This causes the difficultly soluble sodium salt of anthraquinone monosulphonic acid to separate out, leaving the easily soluble salt of the disulphonic acid in solution.

The pasty mass obtained on neutralising with soda is thoroughly pressed, washed with a little water, and then if required pure recrystallised from this solvent. In this way a beautiful brilliant white scaly crystalline mass is obtained, which consists of pure sodium anthraquinone monosulphonate, the so-called ' silver salt ' of the alizarin manufacturer.

The free acid obtained by the addition of an acid to the soda salt crystallises in plates. It is very easily soluble in cold water and alcohol, but almost insoluble in ether.

When fused with caustic soda, this acid (or rather its soda salt) gives first hydroxyanthraquinone $C_6H_4\!<^{CO}_{CO}\!>C_6H_3OH,$ and then alizarin ; and, as will be shown later on, alizarin, when prepared on a manufacturing scale, is invariably formed from the monosulphonic acid of anthraquinone, not from the disulphonic acid as might be expected. The reason for this is that on fusing hydroxyanthraquinone with caustic soda, a continuous process of oxidation and reduction is carried on, the change being represented by the following equation :—

$$C_{14}H_7(ONa)O_2 + NaOH + O$$
Sodium monohydroxyanthraquinonate.

$$= C_{14}H_6\!\begin{pmatrix}ONa\\ONa\end{pmatrix}O_2 + OH_2.$$
Sodium alizarate.
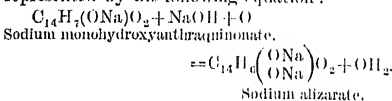
the oxygen being supplied at the expense of a part of the hydroxyanthraquinone which is thereby reduced to anthraquinone. On the large scale this reduction is prevented by the use of chlorate of potash in the fusion.

Literature.—Graebe and Liebermann (Annalen, 160, 131 ; 212, 44 ; Ber. 7, 805).

Anthraquinone disulphonic acids

$$C_6H_4\!<^{CO}_{CO}\!>C_6H_2(SO_3H)_2.$$
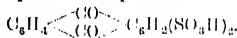
When anthraquinone is heated to a high temperature with 2 or 3 parts of ordinary or better fuming sulphuric acid, a mixture of α- and β-anthraquinone disulphonic acid is obtained, which can be separated by fractional crystallisation of the sodium salts.

Preparation.— 1. A mixture of 10 kilos. of anthraquinone and 20 to 30 kilos. of fuming sulphuric acid is heated to a temperature of 160°–170° until a sample taken out is found to dissolve completely in water. The product is then heated another hour to convert any mono- into disulphonic acid, poured into water, neutralised with caustic soda, and evaporated. 2. 10 kilos. of anthraquinone, 12 kilos. of hydrogen sodium sulphate, and 40 kilos. of ordinary concentrated sulphuric acid are heated in pressure tubes for five or six hours to 260°, the product treated with water, and the acids converted into sodium salts as above.

In concentrating the solution of the sodium salt obtained by either of the above methods, the sodium salt of the α-acid crystallises out first, the more readily soluble salt of the β-acid remaining in the mother-liquors, and thus by

repeated recrystallisation, the two acids are easily separated from one another.

The free acids obtained by decomposing the salts by an acid are both readily soluble in alcohol and water, but insoluble in ether and benzene; the α-acid crystallises in small yellow crystals, the β-acid in beautiful yellow plates.

The salts of the α-acid are sparingly soluble in water and crystallise with difficulty; those of the β-acid are readily soluble and crystallise with the greatest ease.

Besides these two important acids, two other disulphonic acids of anthraquinone are known—viz. χ-anthraquinone disulphonic acid and ρ-anthraquinone disulphonic acid.

Literature.—Schultz (Chemie des Steinkohlentheers, 709, 712); Perkin (Chem. Soc. Trans. 1870, 133); Graebe and Liebermann (Annalen, 160, 134).

χ-Anthraquinone disulphonic acid. This acid is formed by treating sodium α-anthracene disulphonate with nitric acid. The sodium salt crystallises in yellow prisms, which are sparingly soluble in water. On fusing with potash this salt yields chrysazin $C_{14}H_6(OH)_2O_2$, hydroxychrysazin $C_{14}H_5(OH)_3O_2$, m-hydroxybenzoic acid, and salicylic acid.

Literature.—Liebermann and Dehnst (Ber. 12, 1288).

ρ-Anthraquinone disulphonic acid is obtained by oxidising β-anthracene disulphonic acid. The soda salt crystallises in leather-yellow plates, which are easily soluble in water. On fusing with potash it yields anthrarufin

$$(OH) \cdot C_6H_3 <^{CO}_{CO}> C_6H_3(OH),$$
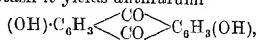
hydroxychrysazin $C_{14}H_5(OH)_3O_2$, m- and o-hydroxybenzoic acids.

Literature.—Liebermann and Dehnst (*l.c.*).

The relation of the various colouring matters of this group to anthracene, anthraquinone, and its sulphonic acids is easily understood from the following table (Schultz):—

```
                                   Anthracene
                                        |
          ┌─────────────────────────────┴─────────────────────────────┐
    Anthraquinone                                   (α- & β-) Anthracene disulphonic acids
          |
  ┌───────┴────────────────┐                                           |
(α- & β-) Monosulphonic acid   (α- & β-) Disulphonic acids    (χ- & ρ-) Disulphonic acids
          |                          α              β                   |
          |                          |              |           ┌───────┴────────┐
o- & m-Hydroxyanthraquinone   Anthraflavic acid   vic acid   Chrysazin       Anthrarufin
          |                          |              |           |                |
      Alizarin                  Flavopurpurin   Isopurpurin   Hydroxy-      (Hydroxyan-
                                              (Anthrapurpurin) chrysazin     thrarufin)
```
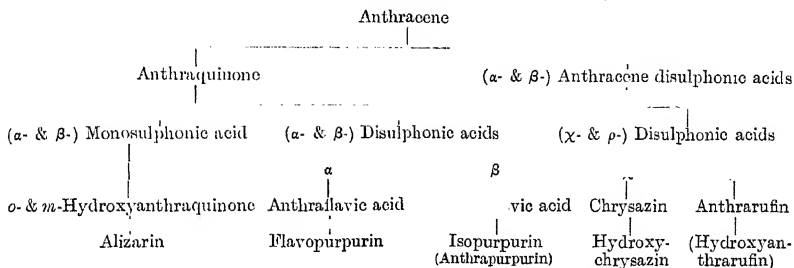
The behaviour of the anthraquinone disulphonic acids on fusion with potash is exactly similar to that of the monosulphonic acid. Just as this acid on fusion with potash is first converted into monohydroxyanthraquinone and then by oxidation into dihydroxyanthraquinone (alizarin), so the anthraquinone disulphonic acids in the first place yield the corresponding dihydroxyanthraquinones, which then by the further action of the potash are converted into trihydroxyanthraquinones.

Hydroxyanthraquinones.

I. Monohydroxyanthraquinones

$$C_6H_4 <^{CO}_{CO}> C_6H_3OH.$$
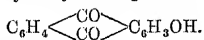
1- hydroxyanthraquinone. Erythroxyanthraquinone.

This substance is formed together with 2-hydroxyanthraquinone by strongly heating a mixture of phenol and phthalic anhydride with sulphuric acid

$$C_6H_4 <^{CO}_{CO}> O + C_6H_5OH$$

$$= C_6H_4 <^{CO}_{CO}> C_6H_3(OH) + H_2O.$$
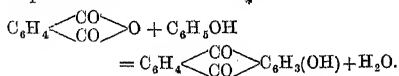
Also by heating 1- bromanthraquinone with potash to 160° or by acting on 1- amidoanthraquinone with nitrous acid in concentrated sulphuric acid solution.

1- hydroxyanthraquinone crystallises from alcohol in orange-red needles which melt at 190°. When fused with potash it gives alizarin. The substance does not dye mordanted fabrics.

1- Acetoxyanthraquinone, prepared by boiling erythroxyanthraquinone with acetic anhydride and sodium acetate, crystallises in yellow needles from alcohol and melts at 176°–179°.

1- methoxyanthraquinone is obtained by the action of boiling methyl alcoholic potash on 1- nitroanthraquinone.

This is the simplest example of a very general reaction in the anthraquinone series. The substance is yellow, microcrystalline, and melts at 140°–145°.

Literature.—Baeyer and Caro (Ber. 7, 969); Pechmann (Ber. 12, 2128); Römer (Ber. 15, 1793); Liebermann and Hagen (Ber. 15, 1804); Hoechste Farbwerke (D. R. P. 97688).

2- hydroxyanthraquinone.

This substance is obtained synthetically (together with erthroxyanthraquinone) by heating a mixture of phenol, phthalic anhydride, and sulphuric acid. The mixed hydroxyanthraquinones can be separated by means of baryta water, since the barium salt of 1- hydroxyanthraquinone is insoluble, whilst the 2- hydroxy compound is easily soluble. It crystallises from alcohol in yellow plates which melt at 323° and readily sublimes at a higher temperature.

It can be obtained in various ways from anthraquinone or its derivatives.

An easy preparation consists in melting anthraquinone sulphonic acid or 2- bromanthraquinone with potash.

The action of ammonium persulphate on a

solution of anthraquinone in concentrated sulphuric acid containing sulphur trioxide leads to the production of 2- hydroxyanthraquinone, alizarin, and purpurin.

Alizarin is reduced to 2- hydroxyanthraquinone by the action of alkaline stannous chloride; or alizarin amide, obtained by the action of ammonia on alizarin, yields this substance when treated with ethyl nitrite.

A very curious reaction of this hydroxyanthraquinone, and one which involves migration of an oxygen atom, is its conversion to quinizarin by treatment with nitrous acid in sulphuric acid solution and in the presence of boric acid.

Literature.—Graebe and Liebermann (Annalen, 160, 141); Baeyer and Caro (Ber. 7, 969); Liebermann and Fisher (Ber. 8, 975); Liebermann (Annalen, 183, 208); Wacker (J. Pr. Chem. [2] 54, 89); Bayer & Co. (D. R. P. 86830).

Dihydroxyanthraquinones.

Alizarin

1 : 2- dihydroxyanthraquinone

$$C_6H_4<^{CO}_{CO}>C_6H_2(OH)_2.$$
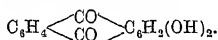
Alizarin occurs in madder as the glucoside ruberythric acid, and also in Chay root (*Oldenlandia umbellata*) and some species of rhubarb.

It is obtained from its glucoside by the action of dilute acids or of ferments.

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$
Ruberythric acid.   Alizarin.   Glucose.
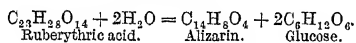
It may be prepared artificially by many methods.

Thus alizarin is produced by fusing dichloranthraquinone, dibromanthraquinone, anthraquinone, mono- or di-sulphonic acids with potash. Rufigallic acid yields alizarin when reduced with sodium amalgam.

On the other hand, anthraquinone may be directly oxidised to alizarin by the action of ammonium persulphate in concentrated sulphuric acid solution.

Good yields of alizarin are said to be obtained by heating anthraquinone with sodium chlorate and a mixture of sodium and potassium hydroxides in aqueous solution at 200°. This process is used for the manufacture of alizarin, but it is not clear that it has entirely displaced the older process shortly to be described.

Hystazarin undergoes isomeric change to alizarin when heated with concentrated sulphuric acid to 200° for two and a half hours.

Alizarin may be synthesised by processes not involving the intermediate formation of anthraquinone.

Together with hystazarin it is produced when a mixture of catechol and phthalic anhydride is heated with sulphuric acid at 200°.

$$C_6H_4<^{CO}_{CO}>O + C_6H_4(OH)_2$$
Phthalic anhydride.   Catechol.

$$= C_6H_4<^{CO}_{CO}>C_6H_2(OH)_21 : 2 + H_2O.$$
Alizarin.
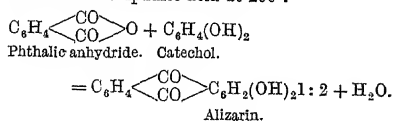
Finally the following synthesis of alizarin is noteworthy:—

Hemipinic anhydride condenses with benzene in the presence of aluminium chloride, yielding the methyl ether of dihydroxybenzoylbenzoic acid. This latter substance, on treatment with hot sulphuric acid, is converted into alizarin methyl ether, which is hydrolysed by aluminium chloride to alizarin. The following formulæ represent this series of reactions:—

Alizarin methyl ether.
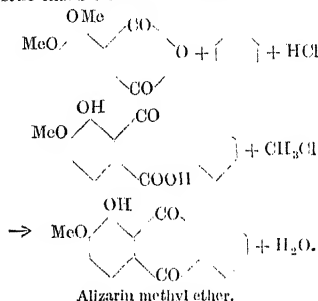
MANUFACTURE OF ALIZARIN.

1. *Anthraquinone process.*—Anthracene, the basis of alizarin, is obtained entirely from the coal-tar oils boiling above 300°, the so-called 'last runnings' of the tar distiller. These heavy oils are redistilled and the anthracene oils collected as soon as the distillate on cooling commences to solidify. In this way a semi-solid greenish-looking mass is obtained, which, after roughly freeing from excess of oil by treatment in hydraulic presses, is the starting-point in the alizarin factory. This crude product contains only about 30—40 p.c. anthracene, the remainder consisting of phenanthrene, naphthalene, carbazol, and small quantities of other hydrocarbons.

The first operation necessary in the manufacture of alizarin is that of purifying the crude anthracene obtained from the tar distillers, in order to obtain a product fit for the subsequent oxidation to anthraquinone.

This process of purification varies considerably in different countries, but the following method may be given as having been used with much success.

The crude anthracene is first ground between edge-runners, and then thoroughly agitated with boiling petroleum spirit in large iron vessels fitted with stirrers and heated with steam.

About 1500 to 1800 lbs. of crude anthracene and 300 gallons of petroleum spirit are used in one operation, the amount of the latter varying slightly according to the quality of the anthracene employed. After boiling for an hour or two, the product is allowed to cool, filtered through coarse canvas, and the anthracene on the filter washed with a little clean petroleum spirit. The pasty mass thus obtained is next treated with steam to remove the excess of petroleum spirit, and then sublimed. The sublimation process is best carried out by melting the anthracene in an iron pot, called the 'subliming pot,' and then blowing in superheated steam. This carries the anthracene vapour forward through a long pipe, where it meets a spray of water, which serves to condense both it and the steam.

The anthracene is thus obtained in an extremely finely divided state, much more suitable for oxidation than when simply ground under edge-runners as it used to be. The next step consists in converting the anthracene into anthraquinone by oxidation with bichromate of potash (or soda) and sulphuric acid—an operation which is usually done in the following way:—The anthracene is placed in lead-lined tanks with about twice its weight of the bichromate (dissolved in water), the requisite amount of dilute sulphuric acid is slowly added, and the mass kept well boiled and agitated by a steam jet connected with a Körting's injector.

The whole is then transferred to settling tanks, the crude yellowish-brown anthraquinone well washed by decantation until free from green chrome liquors, well drained, and freed from water as completely as possible by placing it in canvas bags and exposing it to great pressure in a hydraulic press. The amount of oxidiser required to convert the crude anthracene into anthraquinone is of course regulated by the purity of the sample employed, pure anthracene requiring about 1·66 times its weight of potassium bichromate to convert it into anthraquinone.

Instead of potassium bichromate, the sodium salt is now very often used on account of its cheapness.

The anthraquinone thus obtained is still very impure, and must be carefully purified before it can be converted into sulphonic acid. In purifying anthraquinone two methods may be employed :

(1) The anthraquinone is sublimed, and then recrystallised from high boiling coal-tar naphtha.

(2) The anthraquinone is treated with concentrated sulphuric acid.

When the first process is employed, the anthraquinone is melted in iron pots and subjected to the action of super-heated steam. The steam carries the vapour of the anthraquinone with it, and on condensation a fine, almost impalpable, powder is obtained, which, when dried and recrystallised from high-boiling coal-tar naphtha, consists of nearly pure anthraquinone.

In this country this process has now been almost abandoned ; method (2) having entirely taken its place.

The working of this method is based on the fact that crude anthraquinone when treated with sulphuric acid at 100° dissolves, but is not acted on. The impurities, however, become converted into sulphonic acids, which, being easily soluble, can be removed by treating the product with water, when nearly pure anthraquinone is left behind.

In carrying out this operation a mixture of 1 part of crude anthraquinone and 3 parts of sulphuric acid is placed in large circular lead-lined iron pots, and heated by steam for twenty-four hours, the whole being continuously agitated by a stirrer.

The blackish-looking product is then run into shallow tanks, and exposed to the action of damp air, or a gentle current of steam, until the acid has become diluted. In a short time anthraquinone separates out as a light-brown crystalline powder, which, after washing by decantation, pressing, and thoroughly drying, is found to contain about 95 p.c. of pure substance.

According to recent patents anthraquinone

is best purified by crystallisation from liquid sulphur dioxide or ammonia.

The anthraquinone is now in a condition suitable for conversion into the sulphonic acid.

This operation, which consists in heating anthraquinone with fuming sulphuric acid, is conducted in large iron pots capable of holding from 30 to 40 gallons. The amount of fuming sulphuric acid employed depends on the nature of the sulphonic acid required. In preparing the monosulphonic acid, 1 part of fuming acid (contained 40–50 p.c. SO_3) and 1 to $1\frac{1}{4}$ parts of anthraquinone are used.

The mixture is gradually heated by means of an oil-bath to 170°, or even to 190°, and kept at this temperature for eight or ten hours, the stirrer being kept constantly in motion.

The product, which contains, besides anthraquinonemonosulphonic acid, a little disulphonic acid, and some unacted-on anthraquinone, is diluted with water, passed through a filter-press to remove the anthraquinone, and neutralised with caustic soda.

In a short time the whole becomes quite thick owing to the separation of the sparingly soluble soda salt of anthraquinonemonosulphonic acid, the easily soluble salts of the disulphonic acids remaining in solution.

The crystalline salt is collected in filter-presses, washed with a little very dilute sulphuric acid, and thus obtained practically pure in beautiful, brilliant, pearly scales.

In preparing the disulphonic acids of anthraquinone, the operation is similar to the above, the only difference being that more fuming sulphuric acid is used and the sulphonation conducted at a much higher temperature (about 260°).

The next operation consists in the conversion of the product just described, and called ' soda salt,' into colouring matter, a change which is accomplished by heating it strongly with caustic soda and a little potassium chlorate.

If the potassium chlorate is not added, a considerable loss is incurred owing to the reducing action of a large quantity of nascent hydrogen, always formed during the fusion, which converts the soda salt partially into anthraquinone and hydroanthraquinone. The fusion is conducted in large wrought-iron cylinders fitted with stirrers and heated with hot air. The usual charge is 700 lbs. caustic soda (70 p.c.) dissolved in water, 1300 lbs. of a concentrated solution of ' soda salt,' and 13 to 15 p.c. of potassium chlorate, the amount of this latter substance varying slightly with the nature of the salt used, the monosulphonic salt requiring more chlorate than the disulphonic salt.

The temperature is maintained at about 180° for at least twenty-four hours and often much longer, the progress of the decomposition being controlled from time to time by extracting small quantities of the melt and examining them in the laboratory.

The product thus obtained is an intense purple fluid, becoming thick on cooling and containing the colouring matter as sodium salt besides sodium sulphite and an excess of caustic soda.

To separate the colour the melt is run into large wooden tanks, diluted with water, and boiled with dilute sulphuric acid.

This causes the solution to become orange in colour owing to the precipitation of artificial alizarin.

After being allowed to settle, the supernatant liquor is run off, the alizarin forced into filter-presses and carefully washed until free from acid and saline matter. The colouring matter is then made up to a definite strength (10 p.c. or 20 p.c. paste as required) by transferring it to large wooden tubs fitted with powerful stirrers, and thoroughly mixing it with water.

Pure alizarin thus prepared produces a blue shade of Turkey-red, and anthrapurpurin (produced by fusing sodium anthraquinonedisulphonate with caustic soda) a red shade, so that by varying the amounts of these two constituents any intermediate shade required by the market can be obtained.

2. *Dichloranthracene process.*—In manufacturing alizarin by this process it is necessary, in the first place, to purify the anthracene used much more thoroughly than is the case in the anthraquinone process.

For this purpose the anthracene, after washing with petroleum spirit as described in the last process, is submitted to distillation with potash. This removes the carbazol and the phenolic substances present in the crude anthracene, and as, besides this, a considerable quantity of the other impurities are charred during the distillation, the anthracene resulting, although still very impure, is found to be greatly improved in quality.

In carrying out this operation 100 parts of washed anthracene, 30 parts of potash, and 6 parts of powdered lime are thoroughly ground together under edge-runners, the mixture introduced into iron retorts and distilled. The distillate, which consists of pale-yellow cakes containing about 50 p.c. of pure anthracene, is now sufficiently pure for conversion into dichloranthracene.

In chlorinating anthracene, leaden chambers are used, technically known as 'chlorine ovens.' These are 10 ft. long, 4 ft. 6 in. wide, and 1 ft. 6 in. deep, and are used in pairs, connected at one end in order that any chlorine escaping from the first oven may come in contact with a fresh amount of anthracene and thus prevent loss.

400 lbs. of anthracene are put into each oven, and subjected to the action of a rapid current of chlorine for about five or six hours.

The anthracene first fuses and gets dark in colour, hydrochloric acid being evolved in abundance ; but after a time this fluid product begins to deposit crystals and soon becomes a semi-solid mass. In order to purify this crude product, it is first freed from hydrochloric acid by washing with dilute caustic soda, and then pressed between linen cloths in a hydraulic press, by which means a considerable quantity of a thick dark oily product, technically known as 'chlorine oils,' is got rid of.

The yellow cakes of dichloranthracene thus obtained are still not pure enough for use; they must next be soaked in coal-tar naphtha for some time and pressed, this operation being repeated until a product is obtained which contains 84 p.c. of pure substance.

The next process consists in converting the dichloranthracene into the sulpho- acids of anthraquinone by treating it with ordinary concentrated sulphuric acid. This decomposition is accomplished in iron pots capable of holding about 30 gallons and fitted with iron covers in which there is an opening for the escape of the acid vapours formed during the reaction.

These pots are charged with 350 lbs. of concentrated sulphuric acid and heated to 140°–160° by means of an ordinary fire, the dichloranthracene (70 lbs.) being shovelled in in small quantities at a time. After all the dichloranthracene has been added and the frothing due to the evolution of the hydrochloric and sulphurous acids produced during the decomposition has subsided, the temperature is gradually raised to 260° and then maintained at this point until a sample taken out on a glass rod and diluted with water forms a nearly clear solution devoid of fluorescence.

The product contains now the mono- and disulphonic acids of anthraquinone, the latter of which greatly predominates.

These crude sulphonic acids are next diluted with water in a large wooden tank and boiled with slaked lime until neutralised. The neutral product is then forced into filter presses to separate the calcium sulphate, the clear filtrate mixed with the washing of the calcium sulphate, evaporated until it contains about 15 p.c. of lime salts, and then treated with sufficient sodium carbonate to precipitate all the lime as carbonate.

The solution of the sodium salts of the sulphonic acids is siphoned from the precipitated calcium carbonate, concentrated until it contains 30 p.c. of soda salts, and then converted into colouring matter by fusion with caustic soda, as described in the last process.

Purification of artificial alizarin. Commercial alizarin contains as impurities hydroxyanthraquinone, anthrapurpurin, flavopurpurin, and small quantities of other colouring matters.

In order to separate the alizarin from these, the crude commercial product is dissolved in dilute caustic soda, and the solution treated with carbonic acid until two-thirds of the colouring matter has been precipitated as acid sodium salt. The precipitate is collected, washed with water, decomposed with hydrochloric acid, the crude alizarin thus obtained dissolved in caustic soda, and the treatment with carbonic acid repeated twice more.

The purified product is then boiled with baryta water to remove hydroxyanthraquinone and anthraflavic acid (which dissolve), the barium salt of alizarin is collected, washed, decomposed by hydrochloric acid, and the alizarin either sublimed or recrystallised from alcohol.

Another method of separation is based on the temperatures at which the various constituents of the mixture sublime. Alizarin itself sublimes at 110°, flavopurpurin and anthrapurpurin at 160° and 170° respectively.

Alizarin crystallises from alcohol in red needles or prisms, which melt at 282°. With care alizarin can be sublimed in magnificent deep-red prisms, which, if the operation be performed on a large scale, may be obtained over an inch in length.

It dissolves in alkalis with a purple colour, and is completely precipitated from this solution by the addition of lime or baryta in the form of a blue precipitate of the calcium or barium salt. Heated with acetic anhydride to 160° alizarin forms a diacetyl compound $C_{14}H_6O_2(C_2H_3O)_2O_2$,

which crystallises from alcohol in long yellow needles, melting at 160°. When treated with nitrous acid, alizarin yields anthraquinone. Nitric acid acts violently on alizarin with evolution of red vapours and formation of phthalic and oxalic acids. Distillation with zinc reduces alizarin to anthracene.

When fused with alkaline hydroxides at a fairly high temperature, protocatechuic acid and benzoic acid are formed. Concentrated aqueous ammonia at 200° replaces the hydroxyl in position (1) by amidogen. The 1-amido-2-hydroxy-anthraquinone so produced is called alizarin amide.

Salts of alizarin. *Calcium alizarate*
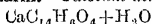
$$CaC_{14}H_6O_4 + H_2O$$

is precipitated by adding calcium chloride to an ammoniacal solution of alizarin as a purple mass. *Barium alizarate* $BaC_{14}H_6O_4 + H_2O$ is prepared, like the calcium salt, by mixing an alkaline solution of alizarin with barium chloride. It is deep-violet when moist, almost black when dry, and very sparingly soluble in water. *Aluminium alizarate* $(C_{14}H_6O_2)_3Al_2O_6(?)$ is obtained by precipitating an alkaline solution of alizarin with alum or aluminium hydroxide. It is a very fine red or rose-red precipitate. *Lead alizarate* $C_{14}H_6O_4Pb$ is obtained by mixing an alcoholic solution of alizarin with an alcoholic solution of sugar of lead.

Alizarin can readily be detected by means of the spectroscope, as it gives in alkaline solution two sharp absorption bands, one at D and one near C, as will readily be seen from the accompanying figure, which shows the absorption
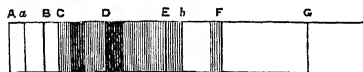
spectrum of a solution of alizarin in alcoholic potash.

Literature. — Anderson (J. 1847-48, 749); Stenhouse (J. 1864, 543); Rochleder (Ber. 3, 295); Perkin (Chem. Soc. Trans. 23, 141); Graebe and Liebermann (Annalen Suppl. 7, 300; Ber. 3, 359); Baeyer and Caro (Ber. 7, 972); Liebermann (Annalen, 183, 206); Liebermann and Dehnst (Ber. 12, 1293); Schunck (Annalen, 66, 187); Wolff and Strecker (Annalen, 75, 8); Lagodzinski (Ber. 28, 1428); Widman (Ber. 9, 856); Liebermann Hohenemser (Ber. 35, 1779); D. R. P. 116526; Perkin (Chem. Soc. Trans. 75, 453).

Derivatives of alizarin. When treated with the ordinary re-agents, such as bromine, nitric acid, &c., alizarin forms a variety of valuable substitution products, some of which are used to a considerable extent as dyeing agents. The most important of these are the following :—

Alizarin methyl ether

$$C_6H_4\text{<}^{CO}_{CO}\text{>}C_6H_2\text{<}^{OH\ (1)}_{OMe.\ (2)}$$
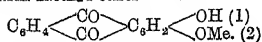
The synthesis of this substance from hemipinic acid has already been described (p. 78).

It can also be produced by treating the monopotassium salt of alizarin with methyl iodide or methyl sulphate.

The substance crystallises from alcohol, and has the melting-point 224°-226°.

The dimethyl ether is not obtained by acting

on the potassium salt of the monomethyl ether with methyl iodide.

Alizarin diethyl ether

$$C_6H_4\text{<}^{CO}_{CO}\text{>}C_6H_2\text{<}^{OEt\ (1)}_{OEt.\ (2)}$$
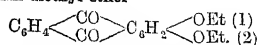
can, however, be prepared by heating alizarin with potash and potassium ethyl sulphate at 160° (Habermann, Monatsh. 5, 228).

Monobromalizarin

$$C_6H_4\text{<}^{CO}_{CO}\text{>}C_6HBr\text{<}^{OH\ (1)}_{OH.\ (2)}$$
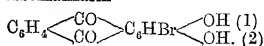
This derivative can be prepared by heating alizarin with bromine and carbon disulphide to 180°-190° for four or five hours.

It is better prepared, however, by sulphonating alizarin with fuming sulphuric acid, and subsequently treating the solution with bromine.

It crystallises from glacial acetic acid in orange-coloured needles, which, when heated, first melt to an orange-coloured liquid and then sublime in orange-red needles.

As a dyeing agent, monobromalizarin retains all the properties of combining with mordants possessed by alizarin, and the colours produced appear to be equally fast. The shade of colour produced is, however, not the same, the reds being less purple, and the purples less blue than those produced by alizarin.

Literature.—Perkin (Chem. Soc. Trans. 27, 401).

α-Nitroalizarin. Alizarin brown

$$C_6H_4\quad\text{>}C_6H\text{<}^{OH\ (1)}_{OH\ (2)}_{NO_2.\ (4)}$$
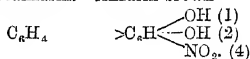
This substance is obtained by treating diacetyl alizarin with nitric acid.

It is manufactured by dissolving alizarin in fuming sulphuric acid and after cooling to −5° to −10°, treating with the calculated quantity of nitric acid dissolved in sulphuric acid.

α-Nitroalizarin crystallises from alcohol or glacial acetic acid in golden-yellow needles. It dissolves in caustic alkali with a blue-violet colour, but if only a minute quantity of alkali is employed the solution is of a fine crimson colour. The alkaline solution gives two absorption bands similar to alizarin. Nitroalizarin is easily reduced in alkaline solution with sodium amalgam or ammonium sulphide and amidoalizarin is the product.

On warming with sulphuric acid 1 : 2 : 3 : 4-tetrahydroxyanthraquinone is produced.

α-Amidoalizarin. Alizarin garnet, Alizarin cardinal

$$C_6H_4\text{<}^{CO}_{CO}\text{>}C_6H\text{<}^{OH\ (1)}_{OH\ (2)}_{NH_2.\ (4)}$$
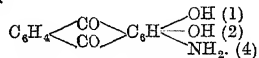
This valuable dye-stuff is obtained by the reduction of α-nitroalizarin. It crystallises from alcohol in small needles of a nearly black colour, but possessing a slight greenish metallic reflection.

Its alcoholic solution gives two absorption bands ; the first is a little beyond D and the second near C. There is also a faint line close to F.

Dyeing Properties of α-Nitro- and α-Amido-alizarin. These colouring matters possess the

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power of dyeing ordinary madder mordants. α-Nitroalizarin gives with alumina mordants very clear orange-red colours, not unlike some of the colours produced with aurin, and with iron mordants reddish-purple colours. Amido-alizarin gives with alumina mordants purple colours, and with iron a bluish or steel-like colour.

It is used for wool-dyeing and calico-printing.

Alizarin Maroon is a mixture of amido-alizarins and purpurins obtained by the reduction of the product of nitration of commercial alizarin in sulphuric acid solution. On alumina mordants it produces a garnet red, maroon on chrome.

Literature.—Perkin (Chem. Soc. Trans. 30, 578); Brasch (Ber. 24, 1610); Schunck and Römer (Ber. 12, 587); D. R. PP. 66811, 74431, 74598.

β-Nitroalizarin, Alizarin Orange

$$C_6H_4 \underset{CO}{\overset{CO}{<}} C_6H \underset{NO_2. \ (3)}{\overset{OH \ (1)}{\underset{OH \ (2)}{<}}}$$
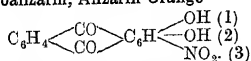
β-Nitroalizarin is prepared by the action of nitric acid on alizarin and also by boiling dinitro-2-hydroxyanthraquinone with caustic soda of 20 p.c.

It is manufactured in large quantities by the action of nitric acid on alizarin dissolved in sulphuric acid containing boric acid. The influence of the boric acid on the position attacked by the nitric acid is probably due to the formation of a boric ester of alizarin.

The crude β-nitroalizarin is purified by crystallisation from glacial acetic acid.

β-Nitroalizarin crystallises in orange-yellow needles which melt with decomposition at 244°. When carefully heated it sublimes, with a good deal of decomposition, in yellow needles. Dissolved in alkalis it forms a purple solution ; the *sodium* salt is insoluble in an excess of caustic soda. The *calcium* salt is an insoluble violet-red precipitate, which is not decomposed by carbonic acid (distinction from alizarin). Treated with glycerol and sulphuric acid, β-nitroalizarin is converted into alizarin blue.

The diacetate of β-nitroalizarin crystallises in yellow needles melting at 218°.

β-Nitroalizarin is prepared on the large scale, and comes into the market under the name of ' Alizarin orange.' In dyeing it is applied to the various fibres in the same way as alizarin ; but although it yields fast colours, it has as yet found only comparatively limited employment. Applied to wool, it gives the following shades:—

With an aluminium mordant it yields a very good orange ; with stannous chloride mordant, a reddish or yellowish orange, according to the amount of mordant used ; with copper sulphate mordant, a good reddish-brown is obtained ; with ferrous sulphate, a purplish-brown ; and with bichromate of potash, a dull brownish-red.

Literature.—Rosenstiehl (Bull. Soc. chim. 26, 63); Schunck and Römer (Ber. 12, 584); Simon (Ber. 15, 692); Bayer & Co. D. R. P. 74562.

Alizarin Red S

$$C_6H_4 \underset{CO}{\overset{CO}{<}} C_6H \underset{SO_3Na.}{\overset{OH \ (1)}{\underset{OH \ (2)}{<}}}$$
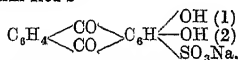
This dyestuff is the sodium salt of the mono-sulphonic acid of alizarin. It is easily prepared by the action of concentrated sulphuric acid on alizarin.

It yields brilliant scarlet red shades with an aluminium mordant, bordeaux red with chromium.

Literature.—Graebe and Liebermann (Annalen, 160, 144).

Alizarin Blue
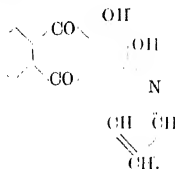
This important colouring matter, discovered by Prud'homme, is obtained by treating β-nitroalizarin with glycerol and sulphuric acid or by treating β-amido alizarin with glycerol, nitrobenzene, and sulphuric acid. Its chemical constitution was first demonstrated by Graebe, who showed that this substance was related to alizarin in precisely the same way as quinoline is to benzene, *i.e.* that alizarin blue is a quinoline of alizarin.

Preparation.— 1 part of β-nitroalizarin, 5 parts sulphuric acid, and 1½ glycerol (of sp.gr. 1·262) are mixed and gently heated.

At 107° the reaction commences and soon becomes very violent, the temperature rising to 200°. After the frothing has subsided, the mass is poured into water, the product well boiled, filtered, and the residue extracted three or four times with very dilute sulphuric acid. The combined extracts on cooling deposit the crude alizarin blue sulphate in brown crystals. These are collected, washed with water till neutral, mixed with water, and borax added until the solution becomes brownish-violet. The precipitate thus formed is filtered off, washed with water, and decomposed with a dilute acid, the crude alizarin blue thus obtained being purified by recrystallisation from benzene or glacial acetic acid.

Alizarin blue crystallises from benzene in brownish-violet needles which melt at 270°, and at a higher temperature gives off orange-red vapours which condense in the form of blue needles.

It is insoluble in water, sparingly soluble in alcohol and ether, more readily soluble in hot benzene. It dissolves in ammonia, potash, or soda, forming blue solutions which become green when mixed with an excess of alkali.

Alizarin blue combines with both bases and acids.

The barium salt $BaC_{17}H_7NO_4BaO + \frac{1}{2}H_2O$ is a greenish-blue precipitate. The following salts of alizarin blue with acids have been prepared :—

$C_{17}H_9NO_4, HCl$ is a red crystalline precipitate formed by passing dry hydrochloric acid gas through a solution of alizarin blue in boiling benzene. When treated with water it is completely decomposed into its constituents. The sulphate crystallises in red needles. The acetate $C_{17}H_9NO_4, C_2H_4O_2$ crystallises in blue plates.

Alizarin blue also combines with picric acid forming a compound $C_{17}H_9NO_4 \cdot C_6H_3(NO_2)_3O$, which crystallises from benzene in long orange-

red prisms melting at 245°. This compound is completely decomposed by water. One of the most important compounds of alizarin blue is the sodium bisulphite compound

$$C_{17}H_9NO_4 \cdot 2NaHSO_3.$$
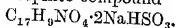
This product is manufactured on a large scale and sold under the name of 'Alizarin Blue S.' It dissolves readily in water, with a brownish-red colour. Alizarin blue is met with in commerce in two forms, viz. as a paste containing about 10 p.c. of dry substance, and as a powder. The former is nearly insoluble in water, while the latter, which is the bisulphite compound (described above), dissolves readily. This soluble kind is now almost entirely used in dyeing. In dyeing cotton with alizarin blue a chromium mordant is used, but in the case of wool, bichromate of potash gives the best results.

Alizarin blue with an alumina or iron mordant is also used for dyeing silk.

Alizarin blue is used largely as a substitute for indigo in calico-printing works. It is one of the most stable colouring matters, and is even said to be faster than indigo itself.

Literature.—Prud'homme (Bull. Soc. chim. 28, 62); Graebe (Annalen, 201, 333); Auerbach (Chem. Soc. Trans. 35, 800).

Alizarin Green S (B).

Alizarin blue can be oxidised by means of sulphur trioxide, and the product on treatment with sulphuric acid gives a dihydroxyalizarin blue of the probable constitution
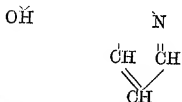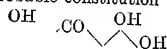
Alizarin Green S (B) is the bisulphite compound of this tetrahydroxyanthraquinone quinoline. It dyes very fast bluish-greens on chromed wool.

Alizarin Indigo Blue S
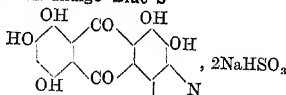
is the bisulphite compound of the pentahydroxy-anthraquinone quinoline, obtained by the further oxidation of alizarin Green S (B) with concentrated sulphuric acid at 200°. It yields fast indigo blue shades on chrome mordanted wool.

Alizarin Green S (M)
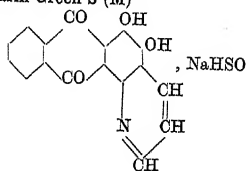
This dyestuff is prepared from *a*-amidoalizarin by treatment with glycerol, nitrobenzene, and sulphuric acid. Its production and properties resemble those of alizarin blue. It is employed in printing, and is used with a nickel magnesia mordant.

Purpuroxanthin. 1 : 3-dihydroxyanthraquinone

$$C_6H_4 {<}{{CO}\atop{CO}}{>} C_6H_2 {<}{{OH\ (1)}\atop{OH.\ (3)}}$$
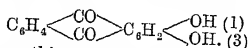
Purpuroxanthin exists in small quantities in madder. It can be prepared by heating purpurin $C_{14}H_6(OH)_3O_2$ with iodide of phosphorus and water, or more readily by boiling purpurin with caustic soda and chloride of tin.

Preparation. — Purpurin is dissolved in a boiling solution of caustic soda (10 p.c.), and chloride of tin added until the solution loses its deep-red tint and becomes of a yellow colour. Hydrochloric acid is then added, the precipitate washed with strong hydrochloric acid, dissolved in baryta water, reprecipitated with hydrochloric acid and crystallised from alcohol.

Purpuroxanthin crystallises in reddish-yellow needles which melt at 262°–263°. It dissolves in alkalis with a reddish colour. If the solution in caustic potash be boiled in the air, it absorbs oxygen, the purpuroxanthin being reconverted into purpurin.

It is not a mordant dyestuff.

Literature.—Schützenberger and Schiffert (Bull. Soc. chim. 4, 12); Liebermann (Annalen, 183, 213); Schunck and Römer (Ber. 10, 172).

Quinizarin. 1 : 4-dihydroxyanthraquinone

$$C_6H_4 {<}{{CO}\atop{CO}}{>} C_6H_2 {<}{{OH\ (1)}\atop{OH.\ (4)}}$$
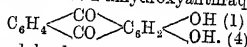
is obtained by heating a mixture of quinol or *p*-chlorphenol and phthalic anhydride with sulphuric acid.

$$C_6H_4 {<}{{CO}\atop{CO}}{>} O + C_6H_4 {<}{{OH\ (1)}\atop{OH\ (4)}}$$
$$= C_6H_4 {<}{{CO}\atop{CO}}{>} C_6H_2 {<}{{OH\ (1)}\atop{OH\ (4)}} + H_2O.$$
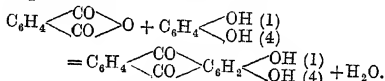
Together with alizarin and purpurin, it is obtained by the action of ammonium persulphate on anthraquinone in sulphuric acid solution; also on heating anthraquinone in sulphuric acid, containing boric acid, with nitrous fumes.

Preparation.—Equal parts of *p*-chlorphenol and phthalic anhydride are heated to 200°–210° for some hours, with ten times as much sulphuric acid as chlorphenol used. The product is poured into two or three times its volume of water, and after standing for twenty-four hours, the precipitate is filtered off, washed and pressed.

The crude product is then boiled with water to free it from phthalic acid, dissolved in caustic soda, precipitated with hydrochloric acid and recrystallised from alcohol. In order to remove a small quantity of purpurin, which is nearly always present, the crude quinizarin is then washed with cold dilute caustic soda as long as the solution is coloured red, and the residue recrystallised from toluene.

Quinizarin crystallises from alcohol in red needles which melt at 192°–193°, and sublime at a high temperature with partial decomposition. It dissolves readily in benzene. The solutions in ether and sulphuric acid are characterised by a beautiful greenish-yellow fluorescence. Quinizarin dissolves in baryta, forming a blue solution

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from which it is reprecipitated on passing carbonic acid (distinction from alizarin).

The tinctorial effects produced by quinizarin on fabrics mordanted with iron, chromium, or aluminium are about $\frac{1}{15}$ of those produced by an equal amount of alizarin.

When fused with potash it is converted into hydroxychrysazin $C_{14}H_8O_5$. Quinizarin forms a diacetate which melts at 200°.

Literature.—Baeyer and Caro (Ber. 8, 152); Schunck and Römer (Ber. 10, 554); Bayer & Co. D. R. P. 81245.

Quinizarin Blue
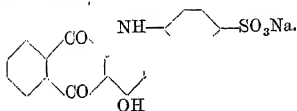
This dyestuff is prepared by heating quinizarin and aniline in molecular proportions and sulphonating the product. From an acid bath it dyes wool a red shade of blue, and gives a greenish blue with chromed wool.

Quinizarin Green.

Quinizarin is treated with an excess of aniline and the product sulphonated. The dyestuff is the sodium salt of the sulphonic acid, and has the constitution
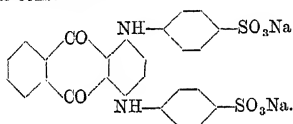
Toluidine and other amines may replace the aniline. The green shades produced on wool from an acid-bath are fast to light and milling.

Hystazarin. Hystazarin, 2 : 3-dihydroxyanthraquinone

$$C_6H_4\!\!<\!\!\begin{array}{c}CO\\CO\end{array}\!\!>\!\!C_6H_2\!\!<\!\!\begin{array}{c}OH\ (2)\\OH.\ (3)\end{array}$$
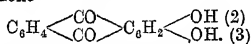
This substance is formed, together with alizarin, when a mixture of pyrocatechol and phthalic anhydride is treated with sulphuric acid—5 grams of pyrocatechol, 6·8 grams phthalic anhydride and 75 grams sulphuric acid are heated for $4\frac{1}{2}$ to 5 hours to 340–150° on a sand-bath.

The resulting product, while still warm, is poured into $\frac{3}{4}$ litre of water, heated to boiling, and filtered hot.

The dark-green precipitate thus obtained is well washed with hot water, dissolved in dilute potash, and the dark-blue solution precipitated by dilute sulphuric acid. The precipitate is washed with water, dried on a porous plate, and treated with boiling alcohol in an extraction apparatus, by which means a considerable portion is dissolved.

The dark-red solution on evaporation yields an orange-red mass, which consists of alizarin and hystazarin. These two substances are readily separated by treatment with boiling benzene, which dissolves the alizarin and leaves the hystazarin; the latter may then be further purified by recrystallisation from acetone.

Yield $1\frac{1}{2}$ p.c. alizarin and 12 p.c. hystazarin of pyrocatechol used.

Hystazarin may be synthesised by the following series of reactions:—Phthalic anhydride condenses with veratrol in carbon disulphide solution under the influence of aluminium chloride.

Phthalic anhydride.   Veratrol.

3 : 4 : dimethoxybenzoyl-
benzoic acid.
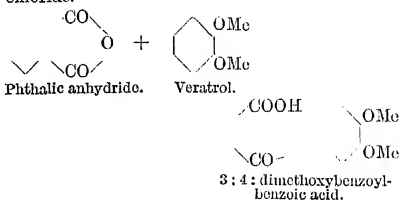
The 3 : 4-dimethoxybenzoylbenzoic acid thus produced yields 2 : 3 : dimethoxyanthraquinone on heating with concentrated sulphuric acid. This is hystazarindimethyl ether and yields hystazarin on demethylation.

Hystazarin crystallises from acetone in orange-yellow needles, which do not melt at 260°.

It is almost insoluble in benzene, difficultly soluble in xylene, soluble in hot alcohol, ether, glacial acetic acid, and acetone.

It dissolves in alkalis with a blue (cornflower) colour, in ammonia with a violet colour, and in concentrated sulphuric acid with a blood-red colour. The barium salt is a blue precipitate, the calcium salt a violet precipitate; both are insoluble in water.

Hystazarin possesses only very feeble tinctorial properties. The faint red colour produced with an aluminium mordant differs in shade from the alizarin red. The solution of hystazarin in dilute sodium hydrate absorbs the yellowish red and violet rays of the spectrum. A very dilute solution shows two lines in the yellow, $\lambda=619\cdot8$, $\lambda_1=587\cdot4$. Distilled over zinc-dust, hystazarin yields large quantities of anthracene.

Diacetyl hystazarin $C_{14}H_6O_2(OC_2H_3O)_2$ crystallises from acetic acid in needles, which melt at 205°–207°.

Literature.— Liebermann and Schoeller (Ber. 21, 2501–2505); Lagodzinski and Lorétan (Ber. 28, 118).

Anthraflavic acid. 2 : 6-dihydroxyanthraquinone

$$(6)\ \ HO\!\cdot\!C_6H_3\!\!<\!\!\begin{array}{c}CO\\CO\end{array}\!\!>\!C_6H_3\!\cdot\!OH.\ (2)$$
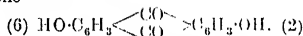
Anthraflavic acid is prepared by fusing α-anthraquinone disulphonic acid with potash, and is therefore nearly always present in artificial alizarin. Synthetically it has been obtained by heating *m*-hydroxybenzoic acid with sulphuric acid to 190°.

$$2OH\!\cdot\!C_6H_4\!\cdot\!COOH$$
$$=OH\!\cdot\!C_6H_3\!\!<\!\!\begin{array}{c}CO\\CO\end{array}\!\!>\!C_6H_3\!\cdot\!OH:H_2O.$$
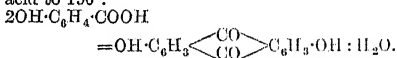
This mode of formation proves that this substance contains the two hydroxyl groups in different benzene rings.

Anthraflavic acid crystallises from alcohol in yellow needles which melt above 330°. The pure substance when carefully heated sublimes partially in yellow needles, leaving a considerable quantity of a carbonaceous residue. Anthraflavic acid does not dye mordanted cloth. It dissolves in alkalis forming a yellowish-red solution, and in sulphuric acid forming a green solution, the

absorption spectrum of which shows a broad band between the blue and the green. Anthraflavic acid forms a number of salts, of which the sodium salt is the most characteristic. This salt is sparingly soluble in water, and is remarkable for the ease with which it crystallises; this distinguishes it from *iso*anthraflavic acid, and gives a ready means of separating these two substances. When treated with acetic anhydride, anthraflavic acid forms a diacetate melting at 228°–229°.

Literature.—Perkin (Chem. Soc. Trans. 1871, 24, 1109; 26, 19); Schunck and Römer (Ber. 9, 379; 11, 970); Liebermann (Ber. 5, 968); Rosenstiehl (Bull. Soc. chim. 29, 401–434); Barth and Senhofer (Ber. 170, 100).

*Iso*Anthraflavic acid. 2 : 7-dihydroxyanthraquinone

(7) $HO \cdot C_6H_3 <^{CO}_{CO}> C_6H_3 \cdot OH$ (2)
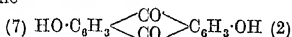
is formed when β-anthraquinone disulphonic acid is fused with potash, and is therefore always contained in crude alizarin. In preparing it, crude alizarin is dissolved in dilute caustic soda, the solution precipitated with hydrochloric acid, and the precipitate dissolved in cold baryta water and filtered. (In this way *iso*anthraflavic acid, which forms a soluble baryta compound, is easily separated from alizarin, anthrapurpurin, and anthraflavic acid, which yield insoluble barium compounds.) The filtrate is treated with hydrochloric acid, and the precipitate recrystallised from alcohol. *Iso*anthraflavic acid crystallises in long yellow needles, containing 1 mol. H_2O, which can be driven off at 150°. It melts above 330° and sublimes at a high temperature in lustrous yellow needles. It dissolves easily in alkalis forming a deep-red solution, but it does not dye mordanted cloth. Fused with potash *iso*anthraflavic acid yields anthrapurpurin.

The diacetate of *iso*anthraflavic acid melts at 195°.

Literature. — Schunck and Römer (Ber. 9, 379).

Anthrarufin. 1 : 5-dihydroxyanthraquinone

(5) $HO \cdot C_6H_3 <^{CO}_{CO}> C_6H_3 \cdot OH$ (1)
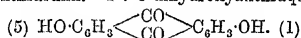
Anthrarufin is formed together with anthraflavic acid and metabenzdioxyanthraquinone by heating *m*-oxybenzoic acid with sulphuric acid.

(2) $OH \cdot C_6H_4 \cdot COOH$

$= OH \cdot C_6H_3 <^{CO}_{CO}> C_6H_3 \cdot OH + 2H_2O$.
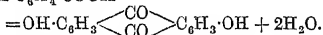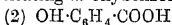
It may also be obtained by fusing *o*-anthraquinone disulphonic acid with potash.

The process employed for the manufacture of anthrarufin depends on the fact that it is the chief product when anthraquinone is oxidized with sulphur trioxide under the following conditions:—Anthraquinone (50 pts.) is heated with fuming sulphuric acid (1000 pts. containing 80 p.c. SO_3) and boric acid (20 pts.) for 36 hours at 100° under pressure.

Anthrarufin crystallises in yellow needles which melt at 280° and sublime easily at a higher temperature (distinction from anthraflavic acid). It dissolves with difficulty in ammonia and soda, but more readily in potash.

Anthrarufin dissolves in sulphuric acid, forming a deep-red solution, the colour of which is so intense that it is still easily apparent in solutions containing only 1 part in 10,000,000.

Anthrarufin forms a diacetate which melts at 244°–245°.

Anthrarufin dimethyl ether is obtained on boiling 1 : 5 : dinitroanthraquinone with methyl alcoholic caustic soda. The substance forms deep-red needles of m.p. 230°.

Literature.—Schunck and Römer (Ber. 11, 1175); Liebermann and Dehnst (Ber. 12, 1289); Bayer and Co. D. R. P. 101220.

Alizarin Saphirol B.
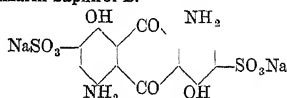
is an important blue acid wool-dye derived from anthrarufin by successive sulphonation, nitration, and reduction. This dyestuff excels in respect to its fastness to light.

Metabenzdioxyanthraquinone. 1 : 7 - dihydroxyanthraquinone

(7) $HO - C_6H_3 <^{CO}_{CO}> C_6H_3 - OH$. (1)
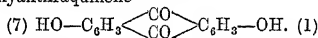
Literature.—Schunck and Römer (Ber. 11, 1176); Liebermann and Dehnst (Ber. 12, 1289).

Metabenzdihydroxyanthraquinone $C_{14}H_8O_4$ is formed together with anthraflavic acid and anthrarufin by heating *m*-hydroxybenzoic acid with sulphuric acid (*v. supra*). It is separated from these by treatment with benzene and subsequent recrystallisation from dilute alcohol. Metabenzdihydroxyanthraquinone forms yellowish needles which melt at 291°–293°, and sublime at a higher temperature almost without decomposition. It dissolves in alkalis with a dark-yellow colour, and in concentrated sulphuric acid, forming a brownish-yellow solution, which shows no absorption bands.

The diacetate of metabenzdihydroxyanthraquinone melts at 199°.

Literature.—Schunck and Römer (Ber. 10, 1225); Rosenstiehl (Ber. 9, 946).

Chrysazin. 1 : 8- or 1 : 6-dihydroxyanthraquinone is formed by fusing χ-anthraquinonedisulphonic acid with potash, or by treating hydrochrysamid $C_{14}H_8(NH_2)_4(OH)_2O_2$ with nitrous acid and alcohol. (N.B.—Hydrochrysamid is obtained by the reduction of chrysammic acid $C_{14}H_4(NO_2)_4O_4$, which is the product of the action of nitric acid on aloes.)

Chrysazin forms reddish-brown needles, which melt at 191°. It dissolves in alkalis and sulphuric acid, with a red colour. Its diacetate melts at 227°–232°.

Crude dinitroanthraquinone contains a compound which is converted into chrysazin dimethyl ether on treatment with methyl alcoholic potash.

Literature.—Liebermann (Annalen, 183, 184).

*Iso*Chrysazin. 1 : 6- or 1 : 8-dihydroxyanthraquinone has been obtained by Lifschütz, by treating dinitroanthraquinone with concentrated sulphuric acid. It crystallises from alcohol and ether in deep-red needles, which melt at 175°–180°. It dissolves in alkalis and in ammonia with a reddish violet colour, and in sulphuric acid with a reddish yellow colour. When heated it sublimes readily, and at a comparatively low temperature, in orange-red plates or needles. It does not dye mordanted cloth.

The *diacetyl compound* melts at 160°–165°.

Literature.—Lifschütz (Ber. 17, 897).

Constitution of the dihydroxyanthraquinones.
The synthesis of quinizarin from phthalic anhydride and quinol establishes its constitution as 1 : 4-dihydroxyanthraquinone

$$\text{,CO. }\quad\text{OH}$$

$$\text{OH}$$

Further alizarin and hystazarin are produced by the condensation of phthalic anhydride with catechol.

It follows that these colouring matters are represented by the following formulæ :—

$$\text{,CO}\quad\text{OH}\qquad\qquad\text{,CO}$$
$$\text{OH}\qquad\qquad\text{OH}$$
$$\text{OH}$$

I.   II.
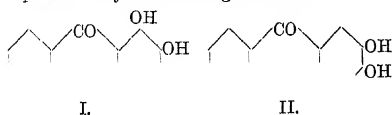
The synthesis of alizarin from hemipinic acid is conclusive evidence that the formula I. represents alizarin, and consequently II. is the structure of hystazarin.

Again, purpurin is produced by the oxidation of both alizarin and quinizarin, and must therefore be 1 : 2 : 4-trihydroxyanthraquinone

$$\text{,CO}\quad\text{OH}$$
$$\text{OH}$$
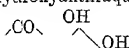
$$\text{OH}$$

On reduction it yields neither alizarin nor quinizarin, but purpuroxanthin, which is obviously 2 : 4-dihydroxyanthraquinone (the same position as 1 : 3).

Similar arguments can be developed with respect to anthraflavic acid, *iso*anthraflavic acid, anthrarufin, and metabenzdioxyanfhraquinone.

There remains a doubt as to the constitution of chrysazin and *iso*chrysazin, but it is most probable that chrysazin is 1 : 8-dihydroxyanthraquinone, in which case the hydroxyl groups in *iso*chrysazin must be in the 1 : 6 position.

The properties of chrysazin are similar to those of anthrarufin, and it is much more probable that dinitroanthraquinone is a mixture of 1 : 8 and 1 : 5 than of 1 : 6 and 1 : 5.

Trihydroxyanthraquinones : Anthrapurpurin, *Iso*purpurin, Hydroxy*iso*anthraflavic acid. 1 : 2 : 7-trihydroxyanthraquinone

$$\text{HO}\quad\text{,CO.}\quad\text{OH}$$
$$\text{OH}$$
$$\text{,CO}$$
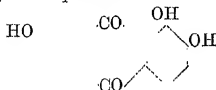
This important colouring matter is contained in crude artificial alizarin. It is formed by fusing β-anthraquinonedisulphonic acid, *iso*anthraflavic acid, metabenzdihydroxyanthraquinone, or α-dibromanthraquinone with potash.

The preparation of this substance is a somewhat tedious process, dependent on the fact that anthrapurpurin differs from alizarin in the behaviour of its alumina lake. The former, on treatment with an alkaline carbonate, is dissolved, whilst the alizarin lake remains unattacked. The solution containing the anthrapurpurin is filtered from the alizarin lake, heated to boiling, and acidified with hydrochloric acid. The anthrapurpurin thus obtained is purified by conversion into its difficultly soluble sodium compound, and from this, by precipitation with barium chloride, the barium salt is obtained, which is decomposed with hydrochloric acid. The precipitate is collected on a filter, well washed with water and recrystallised from glacial acetic acid.

Anthrapurpurin crystallises in orange-coloured needles, which melt above 330°, and, when carefully heated, sublime in long red needles. It dissolves in alkalis with a violet colour ; the solution shows the same absorption spectrum as alizarin.

With acetic anhydride anthrapurpurin forms a triacetate $C_{14}H_5(C_2H_3O)_3O_5$, which crystallises in yellow needles, melting at 220°. When heated with ammonia, anthrapurpurin is converted into anthrapurpurinamide $C_{14}H_5(NH_2)(OH)_2O_2$.

Anthrapurpurin has the same affinity for mordants as alizarin ; the colours it produces are also analogous to some extent, as it produces reds with alumina, purples and blacks with iron mordants. There is, however, a considerable difference in the shade of colour produced, the reds being much purer and less blue than those of alizarin, whilst the purples are bluer and the blacks more intense. When used in Turkey-red dyeing it produces very brilliant colours of a scarlet shade, which are of remarkable permanence.

Literature.—Perkin (Chem. Soc. Trans. 25, 659 ; 26, 425 ; 29, 851) ; Caro (Ber. 9, 682) ; Schunck and Römer (Ber. 9, 679 ; 10, 972, 1823 ; 13, 42) ; Rosenstiehl (Bull. Soc. chim. 29, 405) ; Auerbach (J. 1874, 488).

Purpurin 1 : 2 : 4-trihydroxyanthraquinone

$$\text{,CO}\quad\text{OH}$$
$$\text{OH}$$
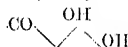
$$\text{OH}$$

Purpurin occurs along with alizarin in madder, probably as a glucoside. In order to separate it from alizarin, the mixture of the two substances is repeatedly recrystallised from a hot solution of alum, in which purpurin is more soluble than alizarin, or the mixture is dissolved in caustic soda and the solution saturated with carbonic acid. This precipitates the alizarin, but not the purpurin.

Purpurin is obtained when alizarin or quinizarin (1 pt.) is heated with pyrolusite (1 pt.) and concentrated sulphuric acid (8–10 pts.) at 160°. The oxidation of alizarin to purpurin is also effected by the action of ammonium persulphate in sulphuric acid containing sulphuric anhydride. α-Amidoalizarin is changed to purpurin by the action of nitrous acid in sulphuric acid solution.

Purpurin crystallises from dilute alcohol in long orange-coloured needles, which contain 1 mol. H_2O. The pure substance begins to sublime at 150°, and melts at 253°. It is slightly soluble in water, forming a deep yellow solution ; in alkalis it dissolves with a purple-red colour ; in alkaline carbonates with a red colour. The solution in alkalis shows two marked absorption bands in the green. Purpurin also dissolves readily in ether, carbon disulphide,

benzene, and acetic acid; these solutions give two absorption bands, one at F and the other near E; the solution in sulphuric acid shows another line in the yellow. When boiled with acetic anhydride it yields a triacetate,

$$C_{14}H_5(C_2H_3O)_3O_5,$$
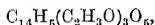
which crystallises in yellow needles, melting a 192°–193°.

Aqueous ammonia at 150° converts purpurin into purpurinamide

$$C_6H_4{<}^{CO}_{CO}{>}C_6H(NH_2)(OH)_2 \quad (OH:OH:NH = 1:3:4),$$
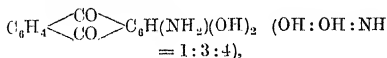
which, when boiled with ethyl nitrite, yields purpuroxanthin,

$$C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{OH\ (1)}_{OH.\ (3)}$$
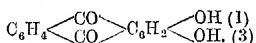
Purpuroxanthin is also the product when purpurin is reduced with either alkaline stannous chloride or sodium amalgam. If, however, zinc-dust be employed as the reducing agent in weakly alkaline, neutral, or acid solution, then the leuco- compound of quinizarin is obtained. Purpurin is converted into 2-anilino-1:4-dihydroxyanthraquinone when heated with a mixture of aniline and aniline hydrochloride. A certain amount of dianilino-hydroxyanthraquinone is produced at the same time.

Purpurin dyes fabrics much in the same way as alizarin and anthrapurpurin, there being, however, a difference in the shades. The reds produced by purpurin are much yellower, and the browns (with chrome mordant) much more intense than are produced either by alizarin or anthrapurpurin.

The following figure shows the absorption spectrum of a solution of purpurin in aluminium sulphate :—

Flavopurpurin. 1 : 2 : 6 - trihydroxyanthraquinone
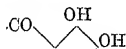
Flavopurpurin occurs in commercial artificial alizarin, but is with difficulty isolated from this product, owing to the fact that its chemical properties agree so closely with those of anthrapurpurin, which is also nearly always present in artificial alizarin, that it can only with difficulty be separated from this substance.

It is prepared by fusing β-anthraquinonedisulphonic acid or anthraflavic acid with potash.

It may be synthesised by the following series of reactions :—

Hemipinic anhydride condenses with anisole in the presence of anhydrous aluminium trichloride, yielding the trimethyl ether of 4 : 5 : 6-trihydroxybenzoyl benzoic acid.

Anisole.　　Hemipinic anhydride.

Trimethoxybenzoylbenzoic acid.
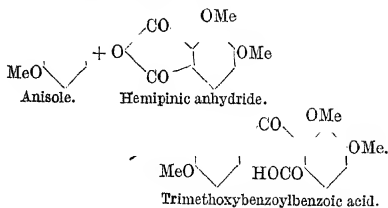
This benzophenone derivative is reduced by zinc-dust and concentrated hydrochloric acid, and the product is 4 : 5 : 6-trimethoxydiphenylmethanecarboxylic acid, which is changed by sulphuric acid to 1 : 2 : 6-trimethoxyanthrone.

4 : 5 : 6-trimethoxydiphenylmethanecarboxylic acid.

1 : 2 : 6-trimethoxyanthrone.
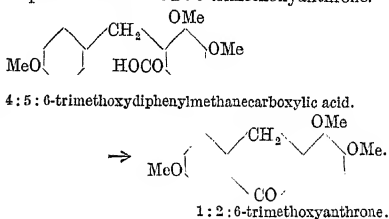
1 : 2 : 6-trimethoxyanthrone crystallises from benzene in small needles melting at 170°. It is oxidised by chromic acid in glacial acetic acid solution to the trimethyl ether of flavopurpurin, which consists of yellow needles, crystallises from acetic acid, and melts at 225°. The trimethyl ether is hydrolysed to flavopurpurin by the action of aluminium chloride at 210°.

Flavopurpurin crystallises from alcohol in anhydrous yellow needles, sparingly soluble in water, but readily soluble in cold alcohol. Its melting-point lies above 330°.

It dissolves in caustic alkalis with a purple colour; the solution shows two absorption bands, one in the blue and the other near the red, but a little further removed than the alizarin band.

Flavopurpurin dyes mordanted fabrics similarly to alizarin, there being, however, a slight difference in the shades produced. The red shade is somewhat duller and yellower; the brown shade is also yellower. Flavopurpurin dyes wool mordanted with tin crystals and cream of tartar a bright yellowish orange.

When heated with acetic anhydride, flavopurpurin yields a triacetate $C_{14}H_5(C_2H_3O)_3O_5$, which crystallises from alcohol in golden-yellow plates melting at 238°.

Alizarin Red 3 W. S. is the sodium salt of the monosulphonic acid of flavopurpurin.

Alizarin Orange G. Nitroflavopurpurin
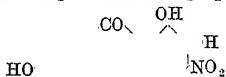
is similarly constituted to β-nitroalizarine. It is obtained by the nitration of flavopurpurin with ordinary nitric acid. Fast orange shades can be produced by applying this compound with an aluminium mordant.

On treatment with glycerol and sulphuric

acid a trihydroxyanthraquinone quinoline of the constitution
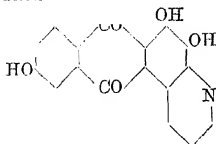
is produced, the bisulphite compound of which is the dyestuff **Alizarin Black P.**

It is used for producing a fast violet grey to black in cotton-printing.

Literature.—Caro (Ber. 9, 682); Schunck and Römer (Ber. 9. 679; 10, 1823 : 13, 42) : Bistrzycki and Yssel de Schepper (Ber. 31, 2798).

Anthragallol. 1 : 2 : 3-trihydroxyanthraquinone
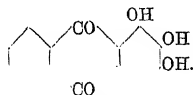
Anthragallol does not itself occur in nature, but its three isomeric dimethyl ethers have been found in Chay root (*Oldenlandia umbellata*). Anthragallol is formed when a mixture of gallic acid (1 pt.), benzoic acid (2 pts.), and sulphuric acid (20 pts.) are heated to 125° for eight hours.
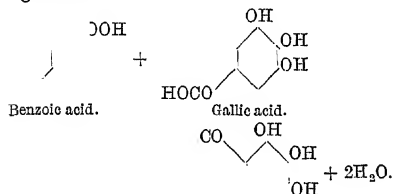
The product is poured into water, well washed, and recrystallised from alcohol.

It is also obtained from 1 : 3-dinitro-2-hydroxyanthraquinone (the nitration product of 2-hydroxyanthraquinone) by reduction in strongly alkaline solution. Or 1 : 3-diamido-2-hydroxyanthraquinone may be converted to anthragallol by heating with hydrochloric acid under pressure.

Anthragallol crystallises in yellow needles which, when heated to 290°, sublime without melting. It is sparingly soluble in water, chloroform, or carbon disulphide ; readily soluble in alcohol, ether, or glacial acetic acid.

It dissolves in alkalis forming a green solution. Its triacetate $C_{14}H_5(C_2H_3O)_3O_5$ melts at 171°–173°.

With an excess of ammonia anthragallol reacts, forming anthragallolamide, 1-amido-2 : 3-dihydroxyanthraquinone.

Literature.—Seuberlich (Ber. 10, 39).

Hydroxyanthrarufin (Hydroxychrysazin).

1 : 4 : 5-trihydroxyanthraquinone. This substance is formed by fusing chrysazin, anthrarufin, ρ- or χ-anthraquinonedisulphonic acids with potash. It crystallises in small red needles, which are sparingly soluble in alcohol. When

strongly heated it sublimes in red needles. It dissolves in potash, forming a violet solution, and shows in its reactions great similarity to purpurin. It differs from this substance in the fact that its solution in alum gives no absorption spectrum.

The solution in sulphuric acid shows, however, two weak bands. The substance is a mordant dyestuff.

The triacetate of hydroxyanthrarufin melts at 192°–193°.

Literature.—Liebermann (Annalen, 183, 191) ; Schunck and Römer (Ber. 11, 1179) ; Liebermann and Boeck (Ber. 11, 1617) ; Liebermann and Dehnst (Ber. 12, 1289).

Tetrahydroxyanthraquinones.

Anthrachrysone. 1 : 3 : 5 : 7-tetrahydroxyanthraquinone
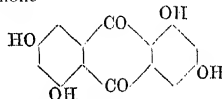
The preparation of this body is effected by heating 3 : 5-dihydroxybenzoic acid with 10 parts of sulphuric acid for 3 to 5 hours.

The substance consists of silky yellow needles when crystallised from alcohol, or it can be sublimed with partial decomposition in leaflets. It does not melt at 360°.

Anthrachrysone has a very feeble affinity for mordants. Its tetraacetate crystallises in yellow needles from acetic acid, and melts at 253°.

Various dyestuffs are derived from anthrachrysone.

Dinitroanthrachrysonedisulphonic acid
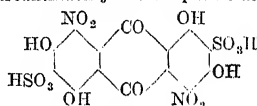
is prepared by sulphonation, followed by nitration of anthrachrysone.

It is a fast brown wool dye.

On reduction it yields diamidoanthrachrysonedisulphonic acid, which dyes wool violet from an acid-bath, or blue on a chromium mordant.

If, however, the reduction is carried out in alkaline solution with sodium sulphide, then the dyestuff **Acid Alizarin Green B and G** results.

The constitution of this product is
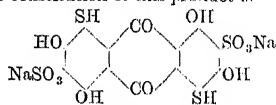
It dyes chromed wool a fast, pure green.

Acid Alizarin Blue BB and GR
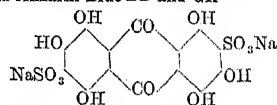
is obtained by boiling diamidoanthrachrysonedisulphonic acid with alkali. A red shade is produced on wool from an acid-bath, which on

chroming develops a beautiful blue, exceedingly fast to light milling, acids or alkalis.

Literature.—Hohenemer (Ber. **35**, 2305); Barth Senhofer (Annalen, 164, 109); Noah (Ber. 19, 755).

Rufiopin.

This tetrahydroxyanthraquinone is obtained by heating opianic or hemipinic acids with sulphuric acid at 180°.

Also by fusing the disulphonic acid of anthrarufin with potash.

It forms a reddish yellow crust from ether, and can be sublimed in orange needles.

It gives a violet-red solution in dilute alkalis or in sulphuric acid. A curious property of rufiopin is its stability towards fusion with potash.

The substance is of no value as a dyestuff, since it gives only dull-brown shades with mordants.

Literature.—Liebermann and Chojnacki (Annalen, 162, 323); D. R. P. 103988.

α- and β-hydroxyanthragallol.

A mixture of these substances is produced when equimolecular proportions of gallic and *m*-hydroxybenzoic acids are heated at 150°, with 10 parts of sulphuric acid for twenty hours.

The product is poured into water and the dried precipitate extracted with alcohol. This extract is evaporated and the residue treated with hot benzene. The α- compound passes into solution, whilst the β- remains undissolved.

α-hydroxyanthragallol crystallises from alcohol in golden yellow micro- needles. It forms a green solution in alkalis, whilst that in sulphuric acid is violet, and shows two absorption bands between F and D. With mordants it behaves similarly to rufigallic acid.

Its tetraacetyl derivative melts at 207°-209°.

β-hydroxyanthragallol crystallises from alcohol and occurs in red needles. Its brown-red solution in sulphuric acid shows two absorption bands between E and H.

The tetra-acetate crystallises from glacial acetic acid in lemon-yellow tablets of m.p. 189°.

Literature.—Noah (Annalen, 241, 270).

1 : 2 : 3 : 4-**tetrahydroxyanthraquinone** is obtained by heating anthragallol with sulphuric acid in the presence of boric acid at 200°-240°. It consists of green needles soluble in both alkalis and sulphuric acid with red colour. The tetraacetyl derivative melts at 205°.

Literature.—Bayer and Co. D. R. P. 86968.

Alizarin bordeaux (Quinalizarin). 1 : 2 : 5 : 8-tetrahydroxyanthraquinone
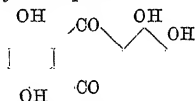
Alizarin bordeaux is by far the most important of the tetrahydroxyanthraquinones.

It has been obtained by the hydrolysis of its dimethyl ether (*see* below) with a solution of hydrochloric acid in acetic acid at 200°.

It is prepared by heating alizarin (1 pt.) with sulphuric acid (10 pts. containing 80 p.c. SO_3) for four days at 25°-50°. This yields the sulphuric acid ester of alizarin bordeaux, to obtain which the reaction product is rendered alkaline and then boiled with an excess of hydrochloric acid.

It is found that the oxidation of alizarin occurs more readily in presence of boric acid.

Alizarin bordeaux can be obtained in deep red needles with green metallic reflection.

On an aluminium mordant it produces bordeaux shades; violet blue on chromium.

The tetraacetate crystallises from chloroform-alcohol in micro- needles of m.p. 201°.

Dimethyl ether of alizarin bordeaux.

This substance is synthesised by heating hemipinic acid and quinol with sulphuric acid to 130°.

The brown-red micro leaflets obtained by crystallisation from benzene melt at 225°-230°.

Literature.—Schmidt (J. pr. Chem. [2] 43, 239); Liebermann and Wense (Annalen, 240, 299).

Pentahydroxyanthraquinones.

Alizarin cyanine R. 1 : 2 : 4 : 5 : 8-pentahydroxyanthraquinone
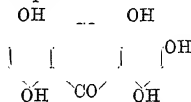
This valuable substance is obtained by the oxidation of alizarin bordeaux with pyrolusite in sulphuric acid solution. The sulphonic acid ether so produced is hydrolysed by boiling with dilute acid. This oxidation is entirely analogous to that by which purpurin is produced from alizarin. The substance crystallises in bronze-coloured leaflets from nitrobenzene. The blue solution in concentrated sulphuric acid exhibits red fluorescence.

Alizarin cyanine R. yields a handsome blue chromium lake.

Dihydroxyanthragallol. 1 : 2 : 3 : 5 : 7-pentahydroxyanthraquinone
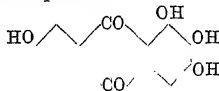
Equimolecular amounts of gallic acid and 3 : 5-dihydroxybenzoic acid are heated to 160° for ten minutes with ten times their weight of sulphuric acid. The product contains dihydroxyanthragallol, rufigallic acid, and anthrachrysone. In order to separate them, advantage is taken of the fact that only dihydroxyanthragallol pentaacetate is soluble in alcohol. The acetate so obtained is hydrolysed with cold sulphuric acid.

Dihydroxyanthragallol crystallises from alcohol in small red needles, which do not melt at 360°. The substance is similar in tinctorial properties to rufigallic acid.

The pentaacetate melts at 229°.

Literature.—Noah (Annalen, 241, 275).

Hexahydroxyanthraquinones. Rufigallol. Rufigallic acid, 1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone

Rufigallic acid is produced when gallic acid is heated with concentrated sulphuric acid at 140°. It may be sublimed in yellow needles. A violet solution is obtained with alkalis, red with sulphuric acid. Baryta produces a blue insoluble precipitate. Alizarin is obtained by the reduction of rufigallic acid with sodium amalgam. The substance is a good example of a polygenetic dyestuff, and yields with aluminium, iron, and chromium mordants, red, violet, and brown respectively. The colours are, however, not pure in tone.

Anthracene Blue. 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone

OH   ,CO   OH
                              ＼OH
                              |
HO·
        OH   ·CO   OH

Anthracene blue is an important dyestuff, and can be obtained from erythroxyanthraquinone, anthrarufin, or anthrachrysone, by the oxidising action of sulphur trioxide in sulphuric acid in the presence of boric acid.

It is best prepared by the action of 40 p.c. sulphuric anhydride on 1 : 5-dinitroanthraquinone, and treatment of the product with ordinary sulphuric acid.

The solution in concentrated sulphuric acid is violet-blue and shows a brown fluorescence. The aluminium lake is violet and the chromium lake blue.

Its disulphonic acid is Acid alizarin blue B B, mentioned above, and prepared from anthrachrysone.

Benzoin Yellow

Ph
|

                                        OH
| ｜   ／ |OH
        CO／

is prepared by the condensation of benzoïn with gallic acid under the influence of sulphuric acid.

It dyes wool on a chromium mordant a fast yellow (except to light).

Gallein $C_{20}H_{12}O_7$

OH   O   OH
O＼／＼／＼／＼OH

＼／＼C
              |
              ／＼
              | |COOH
              ＼／

Galleïn is formed by heating pyrogallol with phthalic anhydride.

Preparation.—A mixture of 1 part of phthalic anhydride and 2 parts of pyrogallol are heated to 190°–200°, the product dissolved in alcohol, and the colouring matter precipitated by the addition of water. The crude galleïn thus obtained is dissolved in alcohol, reprecipitated with water, and, after repeating this operation a few times, converted into the acetate by heating with

acetic anhydride. This is recrystallised several times, and decomposed with potash.

Galleïn crystallises from alcohol in small greenish crystals. It is insoluble in chloroform and benzene, sparingly soluble in water and ether, readily soluble in alcohol, forming a dark-red solution. It dissolves in cold concentrated sulphuric acid without change ; on warming the solution cœrulein is formed.

Galleïn dissolves in small quantities of potash or soda with a red colour ; excess of alkali produces a blue solution. Heated to 150° with acetic anhydride galleïn yields a tetracetate of hydrogalleïn.

Galleïn (often called anthracene violet) is sold in the form of a reddish-brown powder, or a 10 p.c. paste ; not very soluble in cold water, but readily so in hot. With all the usual alizarin mordants galleïn produces purple colours, which are fast to light and soap ; those obtained by the use of chromium and iron are bluish, those with tin reddish, those with aluminium intermediate in tone.

Literature.—Baeyer (Ber. 4, 457 and 663); Buchka (Annalen, 209, 261); Orndorff and Brewer (Amer. Chem. J. 1901, 97).

Cœrulein $C_{20}H_{10}O_6$

O＼   OH   O   OH
  ＼／＼／＼   ＼／＼OH
  | | |
  ＼／＼／＼C／＼／
        CO
        ＼／

Cœruleïn is prepared by heating 1 part of galleïn and 20 parts of sulphuric acid to 200°, and precipitating the colouring matter by adding a large quantity of water. It is thus obtained as a bluish-black mass, which, when rubbed, acquires a metallic appearance. It is almost insoluble in water, ether, and alcohol, more readily soluble in acetic acid.

It dissolves in alkalis with a green colour, in acids with an olive-brown colour. With bisulphite of soda cœruleïn forms an easily soluble compound. With acetic anhydride it forms a triacetate. Cœruleïn (anthracene green) is sold in two forms, either as a bluish-black paste containing 10–20 p.c. cœruleïn, or as a black powder.

The former is insoluble in water, the latter, known as cœruleïn S, is soluble in water, and is indeed a bisulphite compound of cœruleïn.

Cœruleïn is mostly employed in calico-printing for producing very fast olive-green shades. Whatever the mordant used, only different shades of olive-green are produced.

Literature.—Baeyer (Ber. 4, 556, 663); Orndorff and Brewer (Amer. Chem. J. 1901, 97).

W. H. P. and R. R.

ALIZARIN (Natural) *v.* CHAY ROOT and MADDER.

ALIZARIN AND METHYL ETHER *v.* CHAY ROOT.

ALIZARIN BLACK, -BLUE, -BORDEAUX, BROWN, -CARDINAL, -CYANINE, -GARNET, GREENS, -MAROON, -ORANGE, -REDS, -SAPHIROL *v.* ALIZARIN AND ALLIED COLOURING · MATTERS.

ALIZARIN YELLOW *v.* Azo- colouring matters.

ALIZARIN YELLOW A *v.* Ketones.

ALKALI ALBUMIN *v.* Proteins.

ALKALI BLUE. *Nicholson's blue. Sodium triphenyl-rosaniline sulphonate* (*v.* Triphenyl methane colouring matters).

ALKALI BROWNS, -YELLOW *v.* Azo- colouring matters.

ALKALIMETRY *v.* Acidimetry.

ALKALI WASTE *v. Soda manufacture,* art. Sodium.

ALKANET. The Arabic name *Al-henneh,* modified to *alkanna* or *al-kenna,* was originally applied to the lythraceous shrub *Lawsonia alba* (Lam.), the root of which was described as *Radix Alkannæ vera,* in contradistinction to the root of our alkanna, which is *Anchusa tinctoria* (Lam.), and which became known as *Radix Alkannæ spuria tinctoria.* The latter, or *False alkanet,* is also known as *Orcanette,* Fr. ; *Orkanet,* Ger. ; Languedoc bugloss or Dyers' bugloss, *Radix Alkannæ spuria.* A rough plant with downy spear-shaped leaves, and clusters of purplish or reddish flowers; belongs to the *Boraginaceæ.* Found in Asia Minor, Greece, Hungary, &c. The roots, which have an astringent taste, occur in commerce, varying from the thickness of a quill to that of a finger.

Alkanet is one of the more ancient dye-stuffs, having been employed by the Romans, but, on the other hand, it does not appear at any time to have attained such importance as madder, indigo, or even turmeric. The colouring matter of alkanet, known as *anchusin* or *alkannin,* has been examined by several chemists, but it is doubtful whether this compound has as yet been obtained in a chemically pure condition. Its composition is variously given as $C_{17}H_{10}O_4$ (Pelletier, Annalen, 6, 27) $C_{35}H_{20}O_8$ (Bolley and Wydlers, Annalen, 62, 41), $C_{15}H_{14}O_4$ (Carnelutti and Nasini, Ber. 13, 1514), and $C_{15}H_{14}O_4$ or $C_{15}H_{12}O_4$ (Liebermann and Römer, Ber. 20, 2428).

Alkannin forms a dark-red amorphous powder possessing a beetle-green iridescence, is readily soluble in most of the usual solvents, and its alkaline solution is coloured deep-blue. On distillation with zinc-dust it gives, according to Liebermann and Römer, both methylanthracene and anthracene.

Diacetylalkannin $C_{15}H_{12}O_4(C_2H_3O)_2$ forms a dull yellow micro-crystalline powder (C. and N.).

According to Eriksson (Ber. Deut. pharm. Ges. 1910, 20, 202), alkannin consists of two red pigments, the one being coloured green and the other blue by the action of alkalis. Red crystals have been observed by Tschirch in spaces in the cortex of old specimens of alkanet root. As alkannin is insoluble in water, in dyeing with alkanet an alcoholic extract is usually employed ; and with aluminium and iron mordanted fabrics, violet and grey shades are respectively produced. These colours, however, are not fast to light, and are somewhat readily affected by weak alkalis or acids.

Haussmann of Mulhouse introduced alkanet into calico-printing, and for a short time it appears to have played a quite important part, but it is now little if at all employed in Europe for ordinary dyeing purposes. It is still used for colouring artificial wines, pomades, hair-oils,

sweets, &c., and for these purposes it is well adapted on account of its ready solubility and harmless nature.

Böttger (J. pr. Chem. 107, 146) and Eng (J. 70, 935) recommend the use of papers stained by alkanet as indicators in alkalimetry.

According to Jolin (Chem. Schriften über Alkanna, iv. 84), Thompson (Pharm. J. [3] 16, 860), and Eriksson (*l.c.*), alkanet root contains from 5 to 6 p.c. of anchusin. A. G. P.

ALKANNA or **AL-KENNA.** The powdered roots and leaves of the *Lawsonia alba* (Lam.), used in the East for dyeing the nails, teeth, hair, and garments. Used in Persia mixed with lime for dyeing the tails of horses.

ALKANNIN (ANCHUSIN) *v.* Alkanet.

ALKASAL *v.* Synthetic drugs.

ALLANTOIN. *Glyoxyldiureide* $C_4H_6O_3N_4$

$$CO\begin{array}{c}\diagup NH\cdot CH\cdot NH\cdot CO\cdot NH_2 \\ \diagdown NH\cdot CO\end{array}$$

$$\text{or } CO\begin{array}{c}\diagup NH\cdot C:N\cdot CO\cdot NH_2 \\ \diagdown NH\cdot CH\cdot OH\end{array}$$
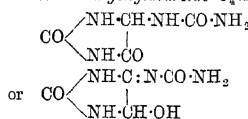
was found originally in the allantoic liquid of cows (Vauquelin and Buniva, Ann. Chim. 23, 269 ; Lassaigne, Ann. Chim. Phys. [2] 17, 301) and in the urine of newly-born calves (Wöhler, Annalen, 70, 229) ; it occurs also in the young leaves, buds, and stem of the plane tree (*Platanus orientalis*) ; sycamore (*Acer pseudoplatanus*), and in the bark of the horse-chestnut (*Æsculus hippocastanum*). Under normal conditions of growth 0·25 gram allantoïn may be isolated from 440 grams of fresh young leaves of the plane, but when the branches are cut in bud and the buds allowed to open in water, the amount of allantoïn increases to 0·5 or 1 p.c. of the dried leaves (Schulze and Barbieri, Ber. 1881, 14, 1602 ; J. pr. Chem. [2] 25, 145 ; Schulze and Bosshead, Zeitsch. physiol. Chem. 1884, 9, 420). It has been found in the nitrogenous constituents of wheat-germs (Richardson and Crampton, Ber. 1886, 19, 1180); in tobacco seeds (Scurti and Perciabosco, Gazz. chim. ital. 1906, 36, ii. 626); and in crude beet juice (*v.* Lippman, Ber. 1896, 29, 2652). Allantoïn is a normal constituent of the urine of mammals; the amount varies in different species, being greatest in the dog and least in man (Frericho, Städeler, J. 1854, 7, 714 ; Wiechowski, Biochem. Zeitsch. 1909, 19, 368 ; Schittenhelm, Zeitsch. physiol. Chem. 1909, 63, 248, 269, 283, 289). In the case of the dog the amount of allantoïn in the urine is increased after a diet of animal food (Salkowski, Ber. 1878, 11, 500), of calf's thymus (Cohn, Zeitsch. physiol. Chem. 1898, 25, 507 ; Mendel, Amer. J. Physiol. 6, xiv.–xv. ; M'Lachlan, Proc. Roy. Soc. Edin. 1906, 26, 95) ; it is also increased after the administration of uric acid (Salkowski, Ber. 1876, 9, 719 ; Swain, Amer. J. Physiol. 1910, 6, 38 ; Wiechowski, Beitr. Chem. Physiol. Path. 1908, 11, 109 ; Biochem. Zeitsch. 1910, 25, 431) or of nucleic acid (Mendel, *l.c.* ; Schittenhelm, Zeitsch. physiol. Chem. 1910, 66, 53 ; Wiechowski, *l.c.*). Allantoïn is therefore to be regarded as an end-product of uric acid metabolism in the case of such animals as dogs and rabbits (Wiechowski, *l.c.* ; Schittenhelm, *l.c.*).

The method of preparation of allantoïn by

oxidising uric acid with lead peroxide in presence of water is due to Liebig and Wöhler (Annalen, 1838, 26, 245); it has been modified by Mulder (Annalen, 1871, 159, 349), who effects the oxidation in dilute acetic acid solution and in bright daylight; by this method 100 grams of uric acid yield 30–32 grams of allantoïn. A quantitative yield of allantoïn is obtained when uric acid is oxidised by an alkaline solution of potassium permanganate, and the intermediate compound

$$CO\begin{Bmatrix} NH\cdot CO\cdot C(OH)\cdot NH \\ | \\ NH ---C(OH)\cdot NH \end{Bmatrix}CO$$
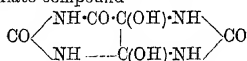
decomposed by acetic acid (Sundvik, Zeitsch. physiol. Chem. 1904, 41, 343; Behrend, Annalen, 1904, 333, 141). Allantoïn is also obtained by the action of nitrous acid on dialuric acid (Gibbs, Annalen Suppl. 1870, 7, 337). The synthesis of allantoïn has been effected (1) by Grimaux (Compt. rend. 1876, 83, 62) by heating a mixture of glyoxylic acid (1 part, and carbamide (2 parts) at 100° for 8–10 hours; (2) by Michael (Amer. Chem. J. 1883, 5, 198) by heating a mixture of mesoxalic acid and carbamide in equal proportions at 110°; (3) and by Simon and Chavanne (Compt. rend. 1906, 143, 51) by the action of ammonia or alkali hydroxides on ethyl allantoate $CH(NH\cdot CO\cdot NH_2)_2CO_2Et$, obtained by the condensation of ethyl glyoxylate with carbamide.

Allantoïn is readily soluble in boiling water, sparingly so in cold (1:131·5 at 21°·8) (Grimaux, Ann. Chim. Phys. 1877, [v] 11, 389); crystallises in glassy monoclinic prisms (Dauber, Annalen, 1849, 71, 511); its heat of combustion at constant pressure is $+ 413·8$ Cal., and heat of formation $+ 170·4$ Cal. (Matignon, Ann. Chim. Phys. 1893, [vi.] 28, 106).

Allantoïn forms a silver salt $C_4H_5O_3N_4Ag$ (Liebig and Wöhler, l.c.) and a potassium salt $C_4H_5O_3N_4K$ (Mulder, l.c.); it also combines with certain metallic oxides to form sparingly soluble compounds; the mercury, copper, zinc, lead, and cadmium derivatives are described by Limpricht (Annalen, 1853, 88, 94). (For the method of estimating allantoïn based on the sparing solubility of the silver and mercury derivatives, see Loewi, Zeitsch. anal. Chem., 1900, 39, 266; Poduschka, ibid. 267.)

Allantoïn is oxidised by potassium ferricyanide in the presence of potassium hydroxide to potassium allantoxanate

$$CO\begin{Bmatrix} NH\cdot CO \\ | \\ NH\cdot C:N\cdot CO_2K \end{Bmatrix}$$
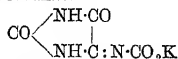
(van Embden, Annalen, 1873, 167, 39); the free acid does not exist, but breaks down, when liberated from its salts, into carbon dioxide and allantoxaïdin

$$CO\begin{Bmatrix} NH\cdot CO \\ | \\ NH\cdot C:NH \end{Bmatrix}$$
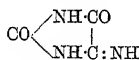
(Ponomareff, Ber. 1878, 11, 2156).   M. A. W.

ALLEMONITE. A native alloy of arsenic and antimony, $SbAs_3$, found at Allemont in the Dauphiné, Przibram in Bohemia; and Andreasberg in the Hartz.

ALLOXAN. Mesoxalylcarbamide

$$CO\begin{Bmatrix} NH\cdot CO \\ NH\cdot CO \end{Bmatrix}C(OH)_2,3H_2O$$
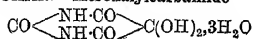
found by Liebig (Annalen, 121, 81) and by Lang (Zeitsch. anal. Chem. 6, 294) in certain pathological excretions, is one of the oxidation products of uric acid, and was first prepared by Brugnatelli (Ann. Chim. Phys. 1817, 8, 201; from Giornale di Fisica, decade seconde i. 117), under the name of erythric acid, by oxidising uric acid by means of nitric acid, chlorine or iodine. Liebig and Wöhler (Annalen, 1838, 26, 256), who systematically studied the oxidation of uric acid, gave to this product the name of alloxan, regarding it as bearing the same relation to allantoïn and oxalic acid that oxaluric acid does to oxalic acid and urea. According to Liebig and Wöhler (l.c.) and to Gregory (Mem. Chem. Soc. 1848, iii. 44), alloxan can be obtained most readily and with a yield of 90 p.c. by careful oxidation of uric acid by means of nitric acid, sp.gr. 1·412.

According to Schlieper (Annalen, 1845, 55, 261), the oxidation of uric acid to alloxan is more conveniently effected with hydrochloric acid and potassium chlorate; 4 parts of uric acid are mixed with 8 parts of hydrochloric acid, and 1 part of finely powdered potassium chlorate added in successive small quantities, avoiding the liberation of chlorine; after two or three hours the dissolved alloxan is reduced by means of sulphuretted hydrogen to the sparingly soluble alloxantin. This is separated from the sulphur by crystallisation from hot water, and oxidised to alloxan by the action of diluted nitric acid.

Alloxan crystallises from warm saturated aqueous solution in large triclinic prisms containing $4H_2O$; on exposure to the air or on heating at 100° it loses $3H_2O$, and the dried compound has the composition expressed by the formula

$$CO\begin{Bmatrix} NH\cdot CO \\ NH\cdot CO \end{Bmatrix}C(OH)_2$$
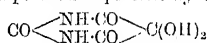
(Lang, Grailich, J. 1858, 308; Hartley, Chem. Soc. Trans. 1905, 87, 1802); it is also obtained in oblique rhombic prisms, belonging to the monoclinic system on evaporating an aqueous solution at 65°–70°. The remaining molecule of water is lost at 150°.

When crystals of alloxan are kept for some years in closed vessels they sometimes undergo spontaneous decomposition, forming alloxantin, parabanic acid, and carbon dioxide. According to Gregory (Annalen, 1853, 87, 126), this is due to the presence of traces of nitric acid contained in the water of crystallisation. Similar phenomena were observed by Baunert (Pogg. Ann. 1860, 110, 93), by Heintz (Pogg. Ann. 1860, 111, 436), and by Otto (Annalen Suppl. 1865, 4, 256). Cases of spontaneous explosive decomposition of alloxan are recorded by Wheeler and by Bogert (J. Amer. Chem. Soc. 1910, 32, 809); the products of decomposition being carbon dioxide, carbamide, oxalic acid, and alloxantin (Gortner, J. Amer. Chem. Soc. 1911, 33, 85).

The molecular heat of combustion of alloxan is 276·5 Cal. (Matignon, Ann. Chem. Phys. 1893, [vi.] 28, 300); the dissociation constant is $2·32 \times 10^{-7}$ (Wood, Chem. Soc. Trans. 1906, 89, 1835). In common with the other simple ureides, alloxan shows no absorption bands in its spectrum (Hartley, Chem. Soc. Trans. 1905, 87, 1815).

Alloxan is readily soluble in alcohol or water;

the solution is acid to litmus, stains the skin purple, and imparts to it a curious and unpleasant odour. In its physiological action alloxan affects the central nervous system, producing first stimulation, then paralysis. When taken internally it is excreted in the urine as alloxantin and parabanic acid (Lusini, Chem. Zentr. 1895, ii. 311, 727, 838; Koehne, Chem. Zentr. 1894, ii. 296).

Alloxan is readily oxidised by warm dilute nitric acid, forming carbon dioxide and *parabanic acid (oxalylcarbamide)* (*q.v.*); is reduced by sulphuretted hydrogen, stannous chloride, zinc, and hydrochloric acid, or by boiling with excess of sulphurous acid to *alloxantin* (*q.v.*); and is readily hydrolysed by alkali carbonates or by the hydroxides or chlorides of the alkaline earths, forming the corresponding salt of *alloxanic acid*. The barium and calcium salts are insoluble.

$$CO\diagdown_{\substack{NH\cdot CO \\ NH\cdot CO}}\diagup CO + H_2O = CO\diagup^{CO\cdot NH\cdot CO\cdot NH_2}_{COOH}.$$
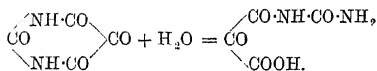
If, however, excess of alkali is employed or the solutions are heated, the hydrolysis is carried to completion with the formation of mesoxalic acid and carbamide (Schlieper, Annalen, 1845, 55, 263; 56, 1). Alloxan gives a deep-blue colour with ferrous salts, but no precipitate is formed unless an alkali is present. According to Agrestini (Boll. Chim. Farm. 1902, 41, 5–7; Chem. Zentr. 1902, i. 631), the formation of blue colour is dependent on the presence of a trace of ammonia or caustic alkali, and the same deep-blue colour is also given by *pure* ferric salts under similar conditions. Alloxan gives the murexide reaction, and Angrestini (*l.c.*) finds that the ammonia in the reaction can be replaced by certain acid amides, amino acids, or substituted amines; Rosenheim's alloxan test for choline (J. Physiol. 1905, 33, 220), namely, the formation of a deep red-violet colour when a drop of a 1 p.c. solution of choline hydrochloride is evaporated on the water-bath with a few drops of a saturated solution of alloxan, is probably a reaction of the same order.

Other tests for alloxan are (1) the formation of a deep violet-blue colour when a solution of alloxan is boiled for a few minutes with a drop of pyrrole. The colour changes to red on cooling, becoming green and then intensely blue on the addition of alkali. (2) The blue-green solution obtained on mixing concentrated sulphuric acid solutions of alloxan (or alloxantin) and pyrocatechol, the colour changes to an intense green on dilution (Agrestini, *l.c.*). Hartley (Chem. Soc. Trans. 1905, 87, 1816) finds that hydrated alloxan, when powdered along with pure calcite, acquires a yellowish-pink tinge. After half an hour the colour is decided and it is permanent; on adding water a red solution is obtained. When alloxan, dried at 100°, is similarly treated, there is no colour developed until water has been added. Alloxanic acid gives no such colour reaction.

The following *homologues* of alloxan have been described:—*Methylalloxan*

$$CO\diagdown_{\substack{NMe\cdot CO \\ NH\_CO}}\diagup CO$$
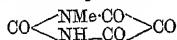
prepared from methyl uric acid (Hill, Ber. 1876,

9, 1092); from ζ-uric acid (Fischer, Ber. 1899, 32, 2731); from theobromine (Maly, Andreasch, Monatsh. 1882, 3, 108; Fischer and Clemm, Ber. 1897, 30, 3090). It crystallises from water in brilliant colourless prisms, becomes anhydrous at 60° in a vacuum, and decomposes at 156°.
Dimethylalloxan

$$CO\diagdown_{\substack{NMe\cdot CO \\ NMe\cdot CO}}\diagup C(OH)_2, H_2O$$
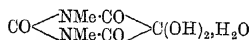
prepared by oxidising caffeine (Fischer, Annalen, 1882, 215, 257; Maly, Andreasch, Monatsh. 1882, 3, 96), by boiling dichlorodimethylbarbituric acid with water or silver oxide (Techow, Ber. 1894, 27, 2083), loses $1H_2O$ when dried over sulphuric acid, decomposes at 100°; the anhydrous compound is a pale yellow powder soluble in alcohol. *Diethylalloxan* $C_8H_{10}O_4N_2$, prepared by oxidising 1:3-diethylbarbituric acid with nitric acid, containing a little nitrous acid (Sembritzki, Ber. 1897, 30, 1820). *Methylethylalloxan*, from ethyltheobromine by oxidation (Pommerehne, Apoth. Zeit. 1897, 12, 5). Some derivatives of 1:3-diphenylalloxan have been described by Whiteley (Chem. Soc. Trans. 1907, 91, 1344).

Inasmuch as the alloxan molecule contains the mesoxalyl radical

$$(OH)_2C\diagdown_{\substack{CO\cdot \\ CO\cdot}} \quad\text{or}\quad OC\diagdown_{\substack{CO\cdot \\ CO\cdot}}$$
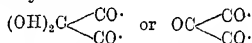
it forms a wide series of condensation products through the medium of the : $C(OH)_2$ or :CO group yielding derivatives of the type

$$R\diagdown C(OH)\diagup_{\substack{CO\cdot NH \\ CO\cdot NH}}\diagup CO \quad\text{or}\quad R:C\diagdown_{\substack{CO\cdot NH \\ CO\cdot NH}}\diagup CO$$
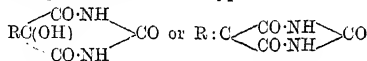
respectively. These compounds will be described under the following eight headings.

1. Condensation of Alloxan with Bisulphites. —Alloxan forms condensation products of the type $C_4H_2N_2O_4, NaHSO_3, 1\frac{1}{2}H_2O$ with alkali bisulphites (Limpricht and Wuth, Annalen, 1858, 108, 41), and with the sulphites of certain organic bases (Pellitzzari, Annalen, 1888, 248, 146). *Alloxan ethylamine sulphite* $C_2H_7N\cdot SO_3H_2\cdot C_4H_2N_2O_4, H_2O$; *Alloxan aniline sulphite* $C_6H_7N\cdot SO_3H_2\cdot C_4H_2N_2O_4, 2H_2O$; *Alloxan methylaniline sulphite* $C_7H_9N\cdot SO_3H_2\cdot C_4H_2N_2O_4\cdot 2H_2O$; *Alloxan dimethylanilinesulphite* $C_8H_{11}N\cdot SO_3H_2\cdot C_4H_2N_2O_4$, $4H_2O$, are described and the crystallographic constants are given. The *benzidine* compound contains $1H_2O$; *toluidine, aminobenzoic acid*, and *aspartic acid* yield similar compounds. *Alloxan pyridine sulphite* is triclinic, and anhydrous crystalline derivatives are afforded by *quino.ine, picoline, morphine*, and *cinchonine*; the *strychnine* compound has $1H_2O$, and the *brucine* compound $1\frac{1}{2}H_2O$.

2. Condensation of Alloxan with Hydroxylamine.—Alloxan condenses with hydroxylamine hydrochloride (Ceresole, Ber. 1883, 16, 1133) to form the *oxime, violuric acid*

$$CO\diagdown_{\substack{NH\cdot CO \\ NH\cdot CO}}\diagup C:N\cdot OH$$
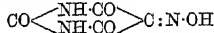
(*q.v.*).

3. Condensation of Alloxan with Hydrazines. —Hydrazones of alloxan and its homologues can be prepared by the condensation of (*a*) the alloxan with the hydrazine

$$CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} CO + H_2N \cdot NHPh$$

$$= CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} C : N \cdot NHPh,$$
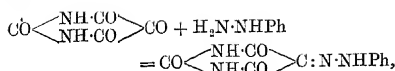
(b) the dibromo- derivative of the corresponding barbituric acid with the hydrazine

$$CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} CBr_2 + H_2N \cdot NHPh$$

$$= CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} C : N \cdot NHPh + 2HBr,$$
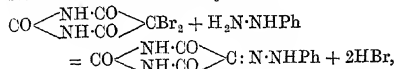
(c) the corresponding barbituric acid with the diazonium chloride

$$CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} CH_2 + ClN_2Ph$$

$$= CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} C : N \cdot NHPh.$$
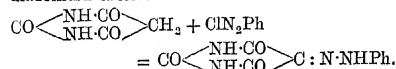
And the following hydrazones have been prepared by one or more of these methods:—*Alloxanphenylhydrazone*

$$CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} C : N \cdot NHPh$$
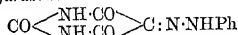
pale-yellow crystals, melts and decomposes at 298°–300° ; 1 : 3-*Dimethylalloxanphenylhydrazone*

$$CO \begin{array}{c} NMe \cdot CO \\ NMe \cdot CO \end{array} C : N \cdot NHPh$$
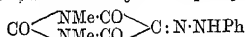
slender yellow crystals, m.p. 261° the *o*- and *p*-nitro derivatives are yellow crystalline substances and decompose at 310° and 300° respectively (Kühling, Ber. 1891, 24, 4140 ; 1898, 31, 1972) ; *alloxanphenylmethylhydrazone*

$$CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} C : N \cdot NMcPh$$
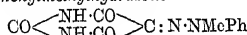
brick-red hexagonal plates, decomposes at 189°–191° (Whiteley, Chem. Soc. Proc. 1906, 22, 201) ; *alloxandiphenylhydrazone*

$$CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} C : N \cdot NPh_2,$$
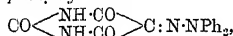
bright-yellow powder, melts above 270° (Armstrong and Robertson, Chem. Soc. Trans. 1905, 87, 1291) ; 1 : 3-*diphenylalloxanphenylhydrazone*

$$CO \begin{array}{c} NPh \cdot CO \\ NPh \cdot CO \end{array} C : N \cdot NHPh$$
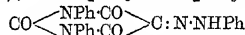
bright-yellow needles that decompose at 265°, the *p-nitro* derivative forms yellow prisms with a purple reflex and melt and decompose at 274° ; 1 : 3-*diphenylalloxanphenylmethylhydrazone*

$$CO \begin{array}{c} NPh \cdot CO \\ NPh \cdot CO \end{array} C : N \cdot NMePh$$
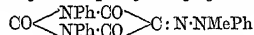
decomposes at 175° and crystallises in orange-red prisms or bright-yellow needles ; 1 : 3-*diphenylalloxandiphenylhydrazone*

$$CO \begin{array}{c} NPh \cdot CO \\ NPh \cdot CO \end{array} C : N \cdot NPh_2$$
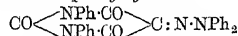
melts and decomposes at 254°–255°, and forms yellow crystals yielding an orange-red powder on trituration ; 1 : 3-*diphenylalloxanphenylbenzylhydrazone*

$$CO \begin{array}{c} NPh \cdot CO \\ NPh \cdot CO \end{array} C : N \cdot NPh \cdot CH_2Ph$$
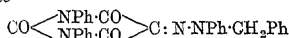
melts and decomposes at 130°, crystallises from benzene in bright-yellow needles, and from methyl alcohol in bright-red prisms ; from toluene a mixture of the red prisms and yellow needles is obtained (Whiteley, Chem. Soc. Trans. 1907, 91, 1344) ; *alloxancyanophenylhydrazone*

$$CO \begin{array}{c} NH \cdot CO \\ NH \cdot CO \end{array} C : N \cdot NPh \cdot CN$$
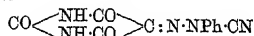
from alloxan and aminophenylcyanamide, straw-yellow compound, m.p. 286° (Rolla, Gazz. chim. ital. 1907, 37, i. 623).

4. Condensation of Alloxan with Semicarbazide.—This reaction has been studied by Bromberg (Ber. 1897, 30, 131). He describes the compounds *alloxansemicarbazide* $C_5H_9O_6N_5$ and *dimethylalloxansemicarbazide* $C_7H_{11}O_6N_5$, but was not successful in determining their constitution.

5. Condensation of Alloxan with Diamines.—In the condensation of alloxan with *o*-diamines the ketonic carbonyl and one of the adjacent carbimido- groups take part, and the product is an *azine* ; *alloxazine*

$$C_6H_4 \begin{array}{c} N : C \cdot NH \cdot CO \\ N : C \cdot CO \cdot NH \end{array}$$
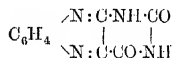
obtained from *o*-phenylenediamine, forms yellow microscopic crystals that decompose above 300° ; similar derivatives were obtained from 3 : 4-diaminotoluene and α-β-diaminonaphthalene (Kühling, Ber. 1891, 24, 2363) ; for the effect of oxidising and reducing agents on these compounds, compare Kühling, Ber. 1895, 28, 1968 ; 1899, 32, 1650).

The condensation of alloxan with mono-substituted *o*-diamines results in the formation of two compounds according as one or more alloxan molecules take part in the reaction. Thus alloxan condenses with *orthaminoditolylamine* at the ordinary temperature to form *alloxanylorthaminoditolylamine*

$$C_7H_7 \cdot NH \cdot C_7H_6 \cdot N : C \begin{array}{c} O \cdot NH \\ CO \cdot NH \end{array} CO$$
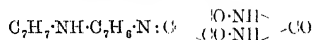
glittering yellow prisms, that melt and decompose at 252°, and dissolve in concentrated sulphuric acid with a deep red colour ; if, however, the condensation is effected in the presence of fuming hydrochloric acid and the mixture is boiled, *dialloxanylorthaminoditolylamine*

$$C(OH) \cdot N(C_7H_7) \cdot C_7H_6 \cdot N : C$$
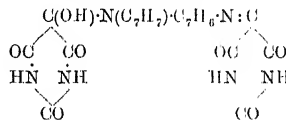
is formed. It is crystalline, and blackens at 300°, dissolves readily in alkali carbonates, and gives a deep-blue solution in concentrated sulphuric acid. Dimethylalloxan gives similar derivatives (Kühling, Ber. 1893, 26, 540), and similar condensation products are obtained from alloxan and phenyl-*o*-phenylenediamine, *o*-aminodi-*p*-tolylamine, and N-methyl-*o*-phenylenediamine (Kühling and Kaselitz, Ber. 1906 ; 39, 1314) ; and from tetramethyl-*m*-phenylenediamine (Sachs and Appenzeller, Ber. 1908, 41, 91).

6. Condensation of Alloxan with Aromatic amines.—Alloxan condenses readily with primary aromatic amines (Pellizzari, Gazz. chim. ital. 1895, 17, 419) to form aminoaryl substituted dialuric acids, yielding on hydrolysis with alkali, the corresponding tartronic acid (*q.v.*). Thus aniline and alloxan give *p*-aminophenyldialuric acid, and this on hydrolysis yields *p*-aminophenyltartronic acid

$$CO\diagdown_{NH\cdot CO}^{NH\cdot CO}\diagup C(OH)_2 + C_6H_5\cdot NH_2$$

$$= CO\diagdown_{NH\cdot CO}^{NH\cdot CO}\diagup C(OH)\cdot C_6H_4\cdot NH_2.$$

$$CO\diagdown_{NH\cdot CO}^{NH\cdot CO}\diagup C(OH)\cdot C_6H_4\cdot NH_2 + 4KOH$$

$$= NH_2\cdot C_6H_4\cdot C(OH)(CO_2K)_2 + 2NH_3 + K_2CO_3.$$
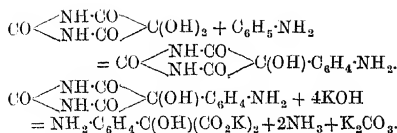
In view of the importance of these compounds as sources of tartronic acids, their preparation forms the subject of a patent, D. R. P. 112174 (Frdl. 1900–1902, 158–159), in which the aminoaryl- dialuric and tartronic acids obtained from the following bases are described : ethylaniline, diethylaniline, benzylaniline, methylbenzylaniline, ethylbenzylaniline, diphenylamine, o-toluidine, o-ethyltoluidine, o-anisidine, methyl-o-anisidine, o-phenetidine, m-chloraniline, m-chlordimethylaniline, and m-chlordiethylaniline.

By careful oxidation with potassium permanganate of the alkali salts of the tartronic acids, or by oxidising the corresponding dialuric acid with mercuric oxide in presence of potassium hydroxide, the corresponding glyoxylic acid (q.v.) can be obtained

$$NH_2\cdot C_6H_4\cdot C(OH)(CO_2H)_2 + O$$
$$= NH_2\cdot C_6H_4\cdot CO\cdot CO_2H + CO_2 + H_2O$$

and the preparation by these methods of an important series of glyoxylic acids forms the subject of patents D. R. P. 117021, 26/11, 1900 ; and 117168, 3/12, 1900.
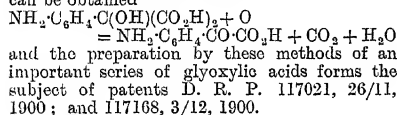
Alloxan condenses also with pyrazolone bases to form derivatives of dialuric acid (tartronylcarbamide), and these on hydrolysis with cold caustic alkali yield the corresponding substituted tartronimides (Pellizzari, Gazz. chim. ital. 1888, 18, 340). Thus *phenylmethylpyrazolonetartronylcarbamide*

$$\begin{array}{l}NPh\cdot CO\\ \mid \qquad\qquad\diagup CH\cdot C(OH)\diagup^{CO\cdot NH}_{CO\cdot NH}\diagdown CO,3H_2O\\ N = CMe\end{array}$$
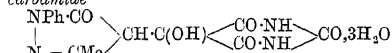
forms long yellow needles that decompose at 170°–178°, and yield *phenylmethylpyrazolonetartronimide*

$$\begin{array}{l}NPh\cdot CO\\ \mid \qquad\qquad\diagup CH\cdot C(OH)\diagup^{CO}_{CO}\diagdown NH\\ N = CMe\end{array}$$

on hydrolysis ; *phenyldimethylpyrazolonetartronylcarbamide*

$$\begin{array}{l}NPh\cdot CO\\ \mid \qquad\qquad\diagup C\cdot C(OH)\diagup^{CO\cdot NH}_{CO\cdot NH}\diagdown CO\\ NMe\cdot CMe\end{array}$$

melts and decomposes at 261°, and yields *phenyldimethylpyrazolonetartronimide*

$$\begin{array}{l}NPh\cdot CO\\ \mid \qquad\qquad\diagup C\cdot C(OH)\diagup^{CO}_{CO}\diagdown NH\\ NMe\cdot CMe\end{array}$$

decomposing at 245°–250°.
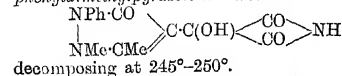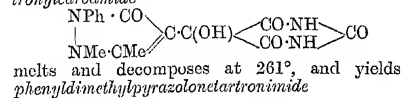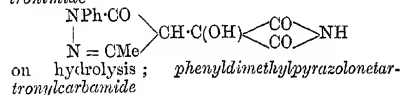
7. Condensation of Alloxan with Phenols.— Alloxan condenses in the presence of hydrogen chloride, sulphuric acid, or zinc chloride with mono- or polyhydroxy- phenols to form derivatives of dialuric acid (tartronylcarbamide), that promise to be of value for pharmaceutical purposes, and are readily converted by hydrolysis into the corresponding tartronic acid :

$$OH\cdot C_6H_5 + (OH)_2C\diagup^{CO\cdot NH}_{CO\cdot NH}\diagdown CO$$

$$\rightarrow OH\cdot C_6H_4\cdot C(OH)\diagup^{CO\cdot NH}_{CO\cdot NH}\diagdown CO$$

$$\rightarrow OH\cdot C_6H_4\cdot C(OH)(CO_2H)_2.$$
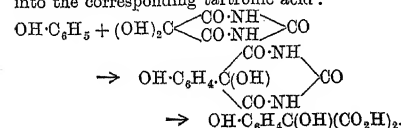
A description of the compounds obtained from alloxan and the phenolic compounds, phenol, m-cresol, p-cresol, guaiacol, pyrocatechol, resorcinol, hydroquinone, pyrogallol, α-naphthol, is given in D. R. P. 107720, 25/8, 1898; 113722, 9/7, 1900 ; 114904, 17/9, 1900 ; and the tartronic acids derived from them are described in D. R. P. 115817, 8/10, 1900.

8. Condensation of Alloxan with Ketones.— Alloxan condenses with acetophenone and certain of its homologues to form phenacyldialuric acid or its derivatives of which the following are described by Kühling (Ber. 1905, 38, 3003), Kühling and Schneider (Ber. 1909, 42, 1285) : *phenacyldialuric acid*

$$COPh\cdot CH_2\cdot C(OH)\diagup^{CO\cdot NH}_{CO\cdot NH}\diagdown CO,H_2O$$
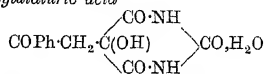
m.p. 212°, with decomposition ; the *bromo*-derivative decomposes at 217° ; *p-ethoxyphenacyldialuric acid* $C_{14}H_{14}O_6N_2$, m.p. 214° ; the *bromo*- derivative, decomposes at 201° ; *αγ-diphenylacetonyldialuric acid*

$$CH_2Ph\cdot CO\cdot CHPh\cdot C(OH)\diagup^{CO\cdot NH}_{CO\cdot NH}\diagdown CO$$
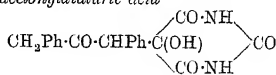
m.p. 233° with decomposition ; *p-methylphenacyldialuric acid*

$$C_6H_4Me\cdot CO\cdot CH_2\cdot C(OH)\diagup^{CO\cdot NH}_{CO\cdot NH}\diagdown CO$$
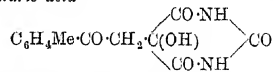
m.p. 241°–242°, with decomposition ; the *acetyl* derivative decomposes at 220°, the *benzoyl* at 215° ; *p-methoxyphenacyldialuric acid* $C_{13}H_{12}O_6N_2$ decomposes at 227°, and yields an *acetyl* derivative, m.p. 207°.   M. A. W.

ALLOXANIC ACID v. **ALLOXAN.**

ALLOXANTIN $C_8H_6O_8N_4, 2H_2O$ (Ritthausen, Ber. 1896, 29, 892) exists in small quantities in crude beet-juice (Lippmann, Ber. 1896, 29, 2645), and forms 34 to 36 p.c. of the products when *convicin* from sow-beans (*Vicia faba minor*) or from vetches (*Vicia sativa*) is hydrolysed by dilute mineral acids (Ritthausen, l.c.; J. pr. Chem. 1899, [ii.] 59, 487). Alloxantin was first prepared by Liebig and Wöhler (Annalen, 1838, 26, 262) by oxidising uric acid with dilute nitric acid ; or by the direct union of alloxan and dialuric acid, or by reducing a cold aqueous solution of alloxan with sulphuretted hydrogen or stannous chloride. According to Vitali (Chem. Zentr. 1898, i. 665, from Boll. Chim. Farm. 37, 65), the reduction can also be effected by means of hydriodic acid. Alloxantin was synthesised by Grimaux (Compt. rend. 1878, 87, 752) by heating malonic acid, carbamide and phosphoryl chloride at 150°, and passing sulphuretted hydrogen through a nitric acid solution of the crude product ; or by passing sulphuretted hydrogen through a hot aqueous solution of dibromobarbituric acid (Compt. rend. 1879, 88, 86). Koech (Annalen, 1901, 315, 246) describes the conversion of *isodialuric* acid into alloxantin by heating it with guanidine and acetic acid ; the change seems to be due to the transformation of the *isodialuric* acid into dialuric acid by the action of the base, and the subsequent oxidation of the dialuric acid to alloxantin, since, if the reaction is conducted in an

atmosphere of carbon dioxide, dialuric acid only is obtained.

Alloxantin crystallises from aqueous solutions in small sharp rhombic prisms, containing 2 mols. H_2O ; it becomes anhydrous after heating for $1-1\frac{1}{2}$ hours at 150°, or for 5 hours at 107°–110° ; it decomposes at 170° into hydurilic acid, ammonia, carbon monoxide, carbon dioxide, and oxalic acid. It is decomposed into barbituric acid and parabanic acid when heated with concentrated sulphuric acid at 120°, or into allituric acid $C_6H_6O_4N_4$ when boiled with excess of hydrochloric acid (Schlieper, Annalen, 1845, 56, 20). Alloxantin is sparingly soluble in cold water, yielding an acid solution that reduces solutions of silver salts, and gives a characteristic violet-blue precipitate with baryta water, changing on warming into the colourless barium alloxanate which undergoes further decomposition into barium mesoxalate and barium carbonate (Liebig and Wöhler, Annalen, 1838, 26, 312). Alloxantin has a molecular heat of combustion = 584·7 Cals. (Matignon, Ann. Chim. Phys. 1893, [6] 28, 323), and a freshly prepared aqueous solution shows a remarkable absorption band in the ultra-violet, which disappears upon keeping the solution, owing to the decomposition of the alloxantin into alloxan and dialuric acid (Hartley, Chem. Soc. Trans. 1905, 87, 1814). For this reason Hartley expresses the constitution of alloxantin by the formula

$$CO\begin{array}{c} \diagup NH\cdot CO \diagdown \\ \diagdown NH\cdot CO \diagup \end{array}\begin{array}{c} \diagup CO\cdot NH \diagdown \\ HO-C\cdot O\cdot C\diagdown-H \\ \diagdown CO\cdot NH \diagup \end{array}CO$$
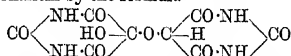
(*ibid.* 1819). Piloty and Finckh (Annalen, 1900, 333, 22) found that alloxantin was resolved into alloxan and dimethylamine dialurate, by boiling with dimethylamine acetate, and suggest the constitutional formula

$$CO\begin{array}{c} \diagup NH\cdot CO \diagdown \\ \diagdown NH\cdot CO \diagup \end{array}\begin{array}{c} HO \diagdown \\ C\cdot O\cdot C \end{array}\begin{array}{c} \diagup C(OH)\cdot NH \diagdown \\ \diagdown CO-NH \diagup \end{array}CO$$
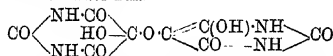
in which the relationship between alloxantin and alloxan is the same as that existing between quinhydrone and quinone.

Alloxantin is readily converted into murexide (*q.v.*) by the action of ammonia, into alloxan by mild oxidising agents, and into dialuric acid by reducing agents. In its physiological action alloxantin resembles alloxan, but is especially poisonous to cold-blooded animals, the blood showing strong reducing properties ; when taken internally it appears in the urine as parabanic acid, and in smaller quantities as dialuric acid, murexide, and alloxantin itself (Kowalewski, Chem. Zentr. 1887, 1296 ; Susini, Ann. Chim. Farm. 1895, 21, 241 ; 1896, 22, 341, 385).

Acetylalloxantin $C_{10}H_8O_8N_4,H_2O$, obtained by the interaction of acetyl dialuric acid and alloxan, crystallises in thin leaflets, becomes anhydrous when kept in a vacuum over sulphuric acid, melts and decomposes at 263°–265°, and is slowly hydrolysed by hot water with the formation of alloxantin.

Benzoylalloxantin $C_{15}H_{10}O_9N_4,H_2O$, similarly formed from benzoyl dialuric acid and alloxan, crystallises in colourless six-sided plates, and melts at 253°–255° (Behrend and Friedrich, Annalen, 1906, 344, 1).

Alloxantin is decomposed when boiled in an

aqueous solution of the hydrochloride of a primary amine, yielding alloxan, together with the corresponding *dibarbiturylalkylamine*. These are colourless crystalline dibasic acids, hydrolysed by boiling with aqueous alkali hydroxides into dialuric acid and the amine. *Dibarbiturylmethylamine*

$$CO\begin{array}{c} \diagup NH\cdot CO \diagdown \\ \diagdown NH\cdot CO \diagup \end{array}C\begin{array}{c} \diagup NMe \diagdown \\ \diagdown H\ H \diagup \end{array}C\begin{array}{c} \diagup CO\cdot NH \diagdown \\ \diagdown CO\cdot NH \diagup \end{array}CO$$
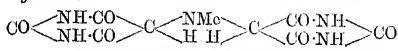
at 280°, *dibarbiturylethylamine* decomposes at 235°, *dibarbiturylphenylamine* becomes blue at 240°, *dibarbituryl-α-naphthylamine* becomes black at 260°, the corresponding β-compound decomposes at 260°, and *dibarbiturylcarbamide* $CO(NH\cdot C_4H_2O_3N_2)_2$ decomposes above 300°.

The following homologues of alloxantin have been prepared : *methylalloxantin* $C_9H_8O_8N_4$, $3H_2O$ from methylalloxan and dialuric acid (Andreasch, Monatsh. 1882, 3, 431) ; *sym-dimethylalloxantin* $C_{10}H_{10}O_8N_4,4H_2O$ from methylalloxan (Maly, Andreasch, Monatsh. 1882, 3, 109), unsym-*dimethylalloxantin* $C_{10}H_{10}O_8N_4$, H_2O from dimethyldialuric acid and alloxan (Andreasch. Montash. 1882, 3, 428). *Tetramethylalloxantin*, $C_{12}H_{14}O_8N_4$ *amalic* acid (from ἀμαλός = soft, so called on account of its feebly acid reaction), prepared (1) by oxidising caffeine with chlorine or nitric acid (Rochleder, Annalen, 71, 1) ; (2) by reducing dimethylalloxan with sulphuretted hydrogen (Fischer, Ber. 1881, 14, 1912) or with stannous chloride (Andreasch, Monatsh. 1895, 16, 19) ; (3) from dimethyldialuric acid and dimethylalloxan (Maly and Andreasch, Monatsh. 1882, 3, 105) ; (4) by the electrolysis of caffeine in sulphuric acid solution (Pommerehne, Arch. Pharm. 235, 365). *Tetraethylalloxantin* $C_{16}H_{22}O_8N_4$, obtained by reducing diethylalloxan, melts and decomposes at 162° (Sembritzki, Ber. 1897, 30, 1821). M. A. W.

ALLOXAZINE *v.* ALLOXAN.

ALLOYS *v.* METALLOGRAPHY.

ALLYL. A univalent radicle C_3H_5—, or $CH_2:CH\cdot CH_2$—, isomeric with *propenyl* $CH_3\cdot CH:CH\diagdown$.

Allyl acetate $CH_3\cdot CO_2C_3H_5$, boils at 103°–104°/733·9 mm. (Brühl), and has sp.gr. 0·9376 at 0° (Schiff). It is only slightly soluble in water, and has a rather sharp smell. It is prepared by the action of allyl iodide on silver acetate (Zinin, Annalen, 96, 361 ; Cahours and Hofmann, Annalen, 102, 295 ; Brühl, Annalen, 200, 179 ; Schiff, Annalen, 220, 109).

Allyl acetic acid $C_3H_5\cdot CH_2\cdot CO_2H$ boils at 187°–189°, and has sp.gr. 0·98416 at 15° (Perkin). It is slightly soluble in water and its smell resembles that of valerianic acid. It is unaffected by reduction with sodium amalgam, but readily unites with two atoms of bromine. It is prepared by hydrolysing allyl acetoacetic acid ethyl ester with dry sodium ethoxide, or by heating allyl malonic acid (Zeidler, Annalen, 187, 39 ; Conrad and Bischoff, Annalen, 204, 170 ; Henry, Chem. Zentr. 1898, ii. 663).

The *chloride* $C_3H_5\cdot CH_2\cdot COCl$ is a thick, pungent-smelling syrup, boiling at 128°/765 mm., and of sp.gr. 1·0739 at 16° (Henry, *l.c.*).

Allylacetone $CH_3\cdot CO\cdot CH_2\cdot C_3H_5$ boils at 128°–130°, and has sp.gr. 0·834 at 27°. It is an unpleasant-smelling liquid. It forms an

amorphous compound with sodium bisulphite, and is reduced by sodium amalgam to hexenyl alcohol. It is prepared by hydrolysing allyl acetoacetic acid ethyl ester (70 grams) with crystallized baryta (215 grams) and water (1650 c.c.) (Zeidler, Annalen, 187, 35; Merling, Annalen, 264, 323). Treated with hydroxylamine it yields *allylacetoxine* $CH_3 \cdot C(:NOH) \cdot CH_2$, C_3H_5, which is a liquid boiling at 188° (corr.), soluble in alcohol, benzene, ether, acids and alkalis.

Allyl alcohol $C_3H_5 \cdot OH$, *i.e.* $CH_2:CH \cdot CH_2 \cdot OH$, occurs in raw wood spirit, but only to the extent of about 0·2 p.c. (Aronheim, Ber. 1874, 1381; Grodzki and Krämer, *ibid.* 1492). It is a pungent liquid with a burning taste, and mixes readily with alcohol, water, or ether. It boils at 96·6° (corr.), and has sp.gr. 0·87063 at 0° and 0·8573 at 15°/15° (Thorpe, Chem. Soc. Trans. 1880, 208).

It is prepared by slowly distilling glycerol (400 pts.) with crystallized oxalic acid (100 pts.) and a little ammonium chloride (1 pt.) to convert any potassium oxalate into chloride. The receiver is changed at 190° and distillation continued up to 260°. The distillate, containing aqueous allyl alcohol, allyl formate, acroleïn, and glycerol, is rectified and dried, first with potassium carbonate, then over solid potash and distilled. When the last traces of water are removed by quicklime it boils at 96°. The yield is one-sixth of the weight of oxalic acid taken (Tollens and Henninger, Bull. Soc. chim. [2] 9, 394; Brühl, Annalen, 200, 174; Linnemann, Ber. 1874, 854). Further purification may be effected by prolonged heating with sodium bisulphite and, after removal of the bisulphite, redistilling several times from quicklime (Thorpe).

It is oxidised by chromic acid solution to acroleïn and formic acid; and by dilute nitric acid to formic and oxalic acids; whilst potassium permanganate produces acroleïn, glycerol, and formic acid. It combines directly with chlorine bromine, iodine chloride, and cyanogen, producing additive products. It is partially reduced by boiling for some hours with zinc and dilute sulphuric acid to *n*-propyl alcohol. Potassium displaces the hydroxylic hydrogen atom and forms gelatinous potassium allylate.

Denigès (Bull. Soc. chim. 1909, 5, 878) describes the following colour reactions for the detection of allyl alcohol, depending on the formation of (1) glyceraldehyde and (2) dihydroxyacetone and the condensation of these products with various reagents. Bromine water (0·6 c.c. in 100 c.c. water) is added to 0·1 c.c. of allyl alcohol, till a slight permanent colouration is produced, and the liquid is then boiled, cooled, and divided into portions of 0·4 c.c. To each of these 0·1 c.c. of a 5 p.c. solution of codeine, resorcinol, thymol, or β-naphthol is added, followed by 2 c.c. of sulphuric acid (sp.gr. 1·84) and the mixture warmed during 3 or 4 minutes at 100°. Codeine and thymol give reddish-violet colourations, resorcinol wine-red, and β-naphthol yellow with greenish fluorescence. The second series of colour reactions is obtained by adding to the brominated liquid above described 5 c.c. of bromine water (0·6 c.c. in 100 c.c. water), heating during 20 minutes at 100°, then boiling

to remove excess of bromine and cooling. This liquid contains dihydroxyacetone, and in the presence of concentrated sulphuric acid gives a deep-blue colour with codeine, orange-red with resorcinol, blood-red with thymol, or green with green fluorescence with β-naphthol (Denigès, Compt. rend. 148, 172 and 282).

Allylamines.

Monoallylamine $C_3H_5 \cdot NH_2$ is a liquid boiling at 53·3° and of sp.gr. 0·7799 at 4° and 0·7688 at 15° (Perkin, Chem. Soc. Trans. 1889, 697); b.p. 58° and sp.gr. 0·864 at 15° (Rinne, Annalen, 168, 262); b.p. 56°–56·5°/756·2 mm. (Schiff, Ber. 1886, 565). It is prepared from allyl *iso*cyanate and potash, or from allyl iodide and ammonia, or by reduction of allyl mustard oil with zinc and hydrochloric acid (Oeser, Annalen, 134, 8). It possesses a penetrating smell, which excites tears and produces sneezing. It is miscible with water in all proportions, and is a strong base, forming a crystalline platinichloride $(C_3H_5 \cdot NH_2)_2 PtCl_6$, and sulphate $(C_3H_5 \cdot NH_2)_2 H_2 SO_4$. The hydrochloride melts at 105°–110° (Delépine, Bull. Soc. chim. [3] 17, 294) and the picrate at 140°–141° after sintering (Gabriel and Eschenbach, Ber. 1897, 1125).

Diallylamine $(C_3H_5)_2 NH$ boils at 111° and is prepared from allylamine and allyl bromide (Ladenburg, Ber. 1881, 1879; Liebermann and Hagen, Ber. 1883, 1641).

Triallylamine $(C_3H_5)_3 N$ is a very unpleasant-smelling liquid, boiling at 150°–151° (Pinner, Ber. 1879, 2054); 155°–156°, sp.gr. 0·8094 at 14·3° (Zander, Annalen, 214, 151). It is prepared by distilling tetrallylammonium bromide with large excess of recently fused potash (Grosheintz, Bull. Soc. chim. [2] 31, 391) or from allyl chloride and alcoholic potassium cyanide in the cold (Pinner, *l.c.*); or from allyl chloride and ammonia (Malbot, Bull. Soc. chim. [2] 50, 90). It is displaced from its aqueous solution by potash, and forms a crystalline platinichloride and hydrochloride.

Tetrallylammonium bromide $(C_3H_5)_4 NBr$ is a crystalline solid, soluble in alcohol and water, but only slightly so in ether. It is prepared by leading a stream of ammonia into an alcoholic solution of allyl bromide. The product is purified by recrystallisation from alcohol containing a little ether (Grosheintz, Bull. Soc. chim. [2] 31, 390). Treated with moist silver oxide it yields tetrallylammonium hydroxide.

Tetrallylammonium iodide $(C_3H_5)_4 NI$ is the main product of the reaction of allyl iodide on ammonia at the ordinary temperature (Cahours and Hofmann, Annalen, 102, 305; Malbot, Ann. Chim. Phys. [6] 13, 488). It is a crystalline solid, insoluble in strong potash solution.

Allylaniline $C_6H_5 \cdot NHC_3H_5$ is a yellow oil produced by the action of allyl iodide on aniline. It boils at 208°–209° and has sp.gr. 0·982 at 25° (Schiff, Annalen Suppl. 3, 364).

Diallylaniline $C_6H_5 \cdot N(C_3H_5)_2$ is prepared by adding allyl bromide (1 mol.) to aniline (1 mol.) in a flask fitted with reflux condenser, separating the allyl aniline by the addition of potash, and converting it into diallyl aniline by repeating the process with more allyl bromide (1 mol.). It boils at 243·5°–245°, and has sp.gr. 0·9538 at 19·8° (Zander, Annalen, 214, 149).

Allyl benzene $C_6H_5 \cdot CH_2 \cdot CH:CH_2$ is obtained by heating together benzene, allyl iodide and

zinc-dust to 100° (Chojnacki, **J.** 1873, **559;** Fittig, Annalen, 172, 132). It boils at 155°. The isomeric *propenyl benzene* (and phenyl propylene—$C_6H_5 \cdot CH:CH \cdot CH_3$) is sometimes incorrectly referred to as allyl benzene.

Allyl bromide, *monobrompropylene* $CH_2:CH \cdot CH_2Br$, boils at 70°–71°, and has sp.gr. 1·4336 at 17° (Zander, Annalen, 214, 144). It is formed by the action of phosphorus tribromide on allyl alcohol, and is prepared by dropping allyl alcohol into a hot solution of potassium bromide in sulphuric acid (1 vol. acid to 1 vol. H_2O) according to Grosheintz (Bull. Soc. chim. [2] 30, 78); or by saturating allyl alcohol with hydrogen bromide at 0° and subsequently heating to boiling for several hours (Jacobi and Merling, Annalen, 278, 11).

Allyl chloride $CH_2:CH \cdot CH_2Cl$ boils at 46°, and has sp.gr. 0·9547 at 0° (Tollens, Annalen, 156, 154); 0·9371 at 19·3° (Zander, Annalen, 214, 142). It is prepared by the action of mercuric chloride on allyl iodide, or from allyl oxalate calcium chloride and alcohol at 100° (Oppenheim, Annalen, 140, 205); or, best, by heating allyl alcohol and concentrated hydrochloric acid to 100° for some hours (Eltekow). It combines with hydrogen chloride to form *propylene chloride* $C_3H_6Cl_2$, and with fuming hydrobromic acid yielding 1-chloro-3-bromopropane $CH_2Cl \cdot CH_2 \cdot CH_2Br$.

Allyl cyanamide, *sinamine*, $C_3H_5 \cdot NH \cdot CN$, is produced by warming allyl thiocarbamide with lead hydroxide on the water-bath (Will, Annalen, 52, 15). On standing for some months crystals separate from the resulting product. It is prepared by shaking an aqueous solution of allyl thiocarbamide with mercuric oxide until the solution no longer blackens ammoniacal silver nitrate (Andreasch, Monatsh. 2, 780). It is alkaline in reaction, precipitating metallic oxides and replacing ammonia in its salts. The crystals contain $\frac{1}{2}H_2O$ and melt at 100°, giving up their water. It forms a difficultly crystallisable salt with oxalic acid, but not with other acids, and double compounds with mercuric and platinic chlorides.

Allyl cyanide, *crotononitrile*, $C_3H_5 \cdot CN$, boils at 119° (corr.), and has sp.gr. 0·8491 at 0° and 0·8351 at 15°. It is obtained by the action of allyl iodide on potassium cyanide, and, together with other products, by allowing allyl mustard oil to remain in contact with water for some weeks, and also by the action of acetic anhydride on crotonaldoxime. It has been prepared by Henry (Chem. Zentr. 1898, ii, 662) by the action of phosphorus pentoxide on *α*- or *β*-hydroxy-butyronitrile. It is a liquid with an unpleasant, onion-like smell. On warming to 50°–60° with fuming hydrochloric acid for two hours, chlorobutyric acid is produced. Chromic acid oxidises it to acetic acid, nitric acid to oxalic acid.

Allylenes. Two allylenes are possible and known: symmetrical allylene $CH_3:C:CH_2$, and unsymmetrical allylene $CH_3 \cdot C:CH$.

Symmetrical allylene, *propadiene*, $CH_2:C:CH_2$, is a gas which burns with a sooty luminous flame. It is prepared by dropping *α*-bromoallyl bromide (10 grams) into a mixture of 20 grams zinc-dust and 25 grams alcohol (70 p.c.) (Gustavson and Demjanow, J. pr. Chem. [2] 38, 202). It does not precipitate ammoniacal solutions of silver nitrate or cuprous chloride. It is readily

absorbed by strong sulphuric acid, and acetone is produced on dilution. When dissolved in absolute ether and heated with sodium to 100°, it changes into the isomeric methyl acetylene. It readily forms a tetrabromide $C_3H_4Br_4$ by addition of bromine.

Unsymmetrical allylene, *methyl acetylene* $CH_3 \cdot C \cdot CH$, results from propylene bromide, monobromopropylene, or monochloropropylene by withdrawal of HCl or HBr by means of alcoholic potash, and from symmetrical allylene (*v. supra*). It is an unpleasant-smelling gas, which is liquefied under a pressure of 3–4 atmospheres. It burns with a bright sooty flame. It dissolves readily in ether (30 vols. in 1 of ether at 16°). Potassium permanganate in the cold oxidises it to formic, oxalic, and malonic acids. Explosive compounds are produced by leading it into ammoniacal solutions of silver nitrate or cuprous chloride. Concentrated sulphuric acid readily absorbs it, forming on dilution and distillation acetone mesitylene and allylene sulphonic acid $C_3H_3SO_3H$ (Schrohe, Ber. 1875, 18 and 367). The *barium salt* of the latter is crystalline, easily soluble, and not decomposed on boiling with water.

Allyl ether $C_3H_5 \cdot O \cdot C_3H_5$ boils at 94·3° and has sp.gr. 0·8046 at 18°. It is prepared from allyl iodide and sodium allyl alcoholate, or from allyl iodide and mercuric oxide (Cahours and Hofmann, Annalen, 102, 290; Berthelot and Luca, Ann. Chim. Phys. [3] 48, 291).

Allyl ethyl ether $C_3H_5 \cdot O \cdot C_2H_5$ boils at 66°–67°/742·9 mm. (Brühl, Annalen, 200, 178). Prepared from allyl iodide and sodium ethoxide.

Allyl iodide C_3H_5I boils at 102·5°–102·8° and has sp.gr. 1·8293 at 23°. Berthelot and Luca, Ann. Chim. Phys. [3] 43, 257) obtained it by the action of PI_3 on glycerol. It may be prepared by leaving together for 24 hours red phosphorus (20 grams), allyl alcohol (160 grams), and iodine (254 grams) (Tollens and Henninger, Annalen, 156, 156); or by the following process: 100 grams of iodine and 1500 grams of carefully dehydrated glycerol are brought together in a large vessel, the air displaced by a current of carbon dioxide, and 300 grams of ordinary phosphorus gradually added. The allyl iodide is distilled off in a stream of carbon dioxide, and then contains as impurity some *iso*propyl iodide. To purify it from this it is dissolved in alcohol and shaken with mercury, when the compound HgC_3H_5I is precipitated. This is recrystallised from water and decomposed, regenerating allyl iodide, by distillation with water and the theoretical quantity of iodine (Linnemann, Annalen Suppl. 3, 263). It combines with bromine to form tribromhydrin, and with hydriodic acid to give diiodopropylene. By long heating with about 20 parts of water it is converted into allyl alcohol and hydriodic acid.

Allyl mercaptan C_3H_5SH boils at 90°. With mercuric chloride it yields C_3H_5SHgCl, which crystallises from alcohol in plates (Hofmann and Cahours, Annalen, 102, 292; Gerlich, Annalen, 178, 88).

Allylmethylal *isothiocyanate* is the name given to the compound $C_3H_5O \cdot S \cdot CH_2 \cdot CN$, prepared by passing a current of formaldehyde gas through glycerol (1 kilo) and allyl *iso*thiocyanate (5 grams) heated to 190° until the weight of the whole is 1400 grams. When cool the product

is filtered and the resulting methylal isothiocya-nate used as an antiseptic (*Pic.*, Fr. Pat. 330988, 1903).

Allyl mustard oil *v.* MUSTARD OIL and ESSEN-TIAL OILS.

Allyl nitrite $C_3H_5NO_2$ is obtained by adding glycerol trinitrite to ice-cold allyl alcohol and cautiously distilling off the allyl ester (Bertoni, *Gazz. chim. ital.* 15, 364). It boils at 43·5°–44·5°, and has sp.gr. 0·9546 at 0°. It is readily decomposed by shaking with water, and yields ethyl nitrite on treatment with ethyl alcohol.

Allyl-phenyl-thiourea $SC{<}^{NH \cdot C_3H_5}_{NH \cdot C_6H_5}$ may be prepared from aniline and mustard oil (Zinin, *Annalen*, 84, 348); or from allylamine and phenyl mustard oil (Weith, *Ber.* 8, 1529). It forms monoclinic crystals, melting at 98°, and is readily soluble in ether, but not in water.

Allyl pyrrol $C_4H_4NC_3H_5$ is readily obtained by the action of allyl bromide on potassium pyrrol in ether (Ciamician and Dennstedt, *Ber.* 1882, 2581). It is a light-yellow oil, turning brown on exposure to air. It boils at 105°/48 mm. It is insoluble in water, but dissolves in HCl, producing a red colour.

Allyl sulphate $C_3H_5 \cdot HSO_4$ is prepared by adding allyl alcohol (1 vol.) to sulphuric acid diluted with its own volume of water (1 vol.), and leaving at ordinary temperatures for five days. Subsequently the mixture is heated to 70° for 12 hours, diluted with water (10 vols.), and saturated with barium carbonate (Szymanski, *Annalen*, 230, 44; *v.* also Cahours and Hofmann, *Annalen*, 102, 293). It forms characteristic salts, a number of which are described by Szymanski (*l.c.*).

Allyl sulphide, *oil of garlic,* (Ger. *Knoblau-chöl*) $(C_3H_5)_2S$, occurs in garlic (*Allium sativum*) and other plants. It is prepared from mustard oil and potassium sulphide at 100° (Wertheim, *Annalen*, 55, 297); or from allyl iodide and potassium sulphide (Hofmann and Cahours, *Annalen*, 102, 291). It is a liquid boiling at 138·6°, and has sp.gr. 0·88765 at 20·8°, 4°. 1 has a very strong odour of garlic and is only slightly soluble in water.

Allyl thiocarbamide, *allyl thiourea, thiosina-mine,* '*Rhodallin*' $SC{<}^{NH_2}_{NH \cdot C_3H_5}$, is produced by the prolonged action of aqueous ammonia on mustard oil (Dumas and Pelouze, *Annalen*, 10, 326). It forms clear six-sided tables, which melt at 78·4°, after sintering at 71°. It is insoluble in benzene, sparingly soluble in water, and readily so in alcohol and ether. It combines directly with halogens, cyanogen, ethyl iodide, acids, &c. Deprived of its sulphur by mercuric oxide, or lead oxide, it yields *sina-mine* (allyl cyanamide) $C_3H_5 \cdot NH \cdot CN$. It has been used in surgery for the removal of scar tissue, being injected as a 10 or 15 p.c. solution in dilute glycerol.

Allyl tribromide, '*Tribromhydrin*' $C_3H_5Br_3$, was obtained by Wurtz by treating allyl iodide with bromine, and by Berthelot and Luca by the action of phosphorus tri- and pentabro-mides on glycerol. It is a slightly yellow liquid of sp.gr. 2·430 at 15·5°, and boils at 217°. It is a strong sedative and anodyne.

Allyl urea $OC{<}^{NH_2}_{NH \cdot C_3H_5}$ crystallizes in needles, melting at 85° (Cahours and Hofmann, *Annalen*, 102, 299; Andreasch, *Monatsh.* 5, 36).

J. A. P.

ALMASCA. A soft grey resin soluble in chloroform, ether, and absolute alcohol. Pro-bably derived from the burseraceous *Protium heptaphyllum* (March.) [*Icica heptaphylla* (Aubl.)] (Symes, *Pharm. J.* [3] 13, 213).

ALMATEIN. Trade name for a condensa-tion product of hæmatoxylin and formaldehyde. Used as an antiseptic.

ALMIRAO. Indian name for *Launæa pinna-tifida* (Cass.) *Microrhynchus sarmentosus* (DC) which belongs to the family Compositæ and is used at Goa as a substitute for taraxacum (Dymock, *Pharm. J.* [3] 6, 730).

ALMOND. The kernel of the fruit of *Prunus amygdalus* or *Amygdalus communis.*

Two principal varieties exist—the sweet and the bitter almond. Both contain amygdalin, but the latter is much richer in this substance (2 to 3 p.c.), and contains an enzyme, *emulsin*, which, in the presence of water, decomposes the amygdalin, yielding glucose, benzaldehyde, and hydrocyanic acid

$C_{20}H_{27}NO_{11} + 2H_2O$
$$= C_6H_5CHO + HCN + 2C_6H_{12}O_6.$$
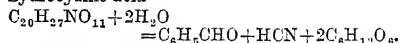
In addition, almonds contain about 50 p.c. of their weight of a fixed oil (mainly olein, and liable to become rancid) and smaller quantities of proteïns, sugar, starch, gum, fibre, and ash.

Analyses of almonds made at various stages of growth and ripening, show the percentage of amyloses, glucose, and saccharose to steadily diminish, whilst the proportion of oil increases (Du Sablon, *Compt. rend.* 1896, 123, 1084).

According to Vallée (*Compt. rend.* 1903, 136, [2] 114), reducing sugars in the immature almond decrease as the fatty oil increases; sucrose increases until oil-formation begins, then decreases during oil-production, and towards the end again increases. Ripe almonds contain about 3 p.c. of sucrose. According to Osborne and Campbell (*J. Amer. Chem. Soc.* 1896, 18, 609), the proteïn in almonds is *amandin* and not conglutin or vitellin.

H. I.

ALMOND OIL is obtained from the seeds of *Prunus amygdalus* (Stokes) [*Amygdalus communis,* (Linn.)]. The almond tree appears to have been indigenous to Turkestan and Middle Asia, and has been transplanted from there to Greece, Italy, Spain, France, and to Northern Africa. The mean percentage composition of the almond is given by König as follows :—

Oil	.	.	.	.	41·00 p.c.
Water	.		.	.	27·72 ,,
Albuminoids		.	.	.	16·50 ,,
Extracted matter, free from nitro-					
gen	.	.	.	.	10·2 ,,
Crude fibre	.	.	.	.	2·81 ,,
Ash	.	.	.	.	1·77 ,,

100·00

The commercial oil is chiefly expressed from bitter almonds, the seeds of *Prunus amygdalus,* var. *amara.* Bitter almonds contain, besides the oil, amygdalin and emulsin, which give rise to the formation of benzaldehyde, glucose, and hydrocyanic acid. Hence the press-cakes

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from almonds find a profitable outlet in the manufacture of genuine ' ethereal bitter almond oil,' by triturating the meal with water.

Sweet almonds (from *Prunus amygdalus,* var. *dulcis*) are but rarely used alone for the preparation of almond oil. Mogador bitter almonds, which are chiefly used in this country for the manufacture of almond oil, are always more or less mixed with sweet almonds. Sweet almonds yield from 44–55 p.c. of oil, bitter almonds yield less and may contain as low a proportion of oil as 20 p.c. On an average, however, bitter almonds yield from 38 to 45 p.c. of oil.

The oil is pale yellow; it has a very pleasant, mild taste, and is almost free from odour. The specific gravity of the oil varies from 0·917 to 0·9195 at 15°. The oil solidifies at −15°, has the saponification value of the majority of oils which are free from volatile acids, and an iodine value of 93–100. This points to the presence of linolic acid, of which about 10 p.c. may be contained, on an average, in almond oil, the remainder being practically oleic acid, since the oil contains no stearic acid, and is most likely also free from palmitic acid.

Almond oil is chiefly used in pharmaceutical practice. Owing to its high price almond oil is largely adulterated with other oils of the *Prunus* family, chiefly with apricot kernel oil, from *Prunus armeniaca* (Linn.), and with peach kernel oil, from *Prunus persica* (Sieb. et Zucc.). These two oils are very similar to almond oil; they differ from it by their higher iodine values, and in having a less pleasant taste than almond oil. They are used to such an extent as adulterants that frequently they completely substitute almond oil; indeed ' foreign' almond oil, or ' oil of sweet almonds, French ' (*Oleum amygda-larum gallicum*), is nothing else than a mixture of apricot kernel oil and peach kernel oil. Genuine almond oil is sold in commerce under the name ' almond oil, English.'

The close relationship in which apricot and peach kernel oils stand to almond oil, renders their detection in almond oil a difficult problem. For methods of solving it the reader is referred to Lewkowitsch, Chemical Technology and Analysis of Oils, &c. ii. 234.   J. L.

ALMONDS, BITTER, *Essential oil of* (*v.* BEN-ZALDEHYDE; *v.* OILS, ESSENTIAL).

ALOË. A genus of succulent plants, having stiff, pointed, fleshy leaves, belonging to the Liliaceæ. (Plants figured, and structure of leaves described, Pennetier, 560, 579.) Of the 85 species 60 are natives of Cape Colony, and the other species are mainly sub-tropical African, though a few occur in the tropics; a number of species have been, however, introduced into the West and East Indies. (For a list of the species and their distribution, *v.* Pharm. J. [3] 11, 746.)

The fibre is used for rope, &c.; experiments made in Paris have shown it to be five times as strong as hemp. The fibre has also been used for paper-making (Nat. 20, 484).

ALOË RESINS *v.* ALOES OR BITTER ALOES.

ALOES or BITTER ALOES. (*Aloès,* Fr.; *Aloë,* Ger.) The inspissated juice or extract of the aloe. The principal varieties found in the market are :—

1. *Barbados Aloes* (aloes in gourds. The juice of *A. vera* (Linn.) growing in Barbados,

Jamaica, and St. Helena. It is opaque, lustre-less, and of a brown colour, with a bitter nauseous taste and very disagreeable odour it gives a powder of a dull-yellow colour.

2. *Cape Aloes* (*A. Perryi, A. lucida ?*), obtained from *A. spicata, A. africana, A. ferox,* and other Cape species. Its odour is stronger and more disagreeable than that of Barbados aloes; it is of a deep greenish-brown colour, is resinous and shining, and its powder is of a greenish-yellow colour, and is almost completely soluble in boiling water.

3. *Hepatic Aloes.* Imported from Bombay and Madras. It is probably the juice of the Socotrine aloe solidified without the aid of arti-ficial heat (Pereira, Pharm. J. [3] 11); it is of an opaque liver colour, its powder contains much matter insoluble in weak alcohol.

4. *Socotrine Aloes.* The juice of *A. Perryi* (Baker) imported from Bombay and Madras. It is of a garnet-red to golden-red colour, is aro-matic, and has an intensely bitter taste; its powder is of a bright golden-yellow colour (Cooley, 1).

5. *Zanzibar Aloes,* from Zanzibar.

Aloïns. By extracting aloes with water the purgative principles, aloïns, can be obtained. Shenstone (Pharm. J. [3] 13, 461; Chem. Soc. Trans. 44, 480) divides them into two classes : 1. *Nataloïns,* which only yield picric and oxalic acids with nitric acid, and which are not reddened by it, even on heating (Flückiger, Arch. Pharm. [2] 149, 11; Tilden, Chem. Soc. Trans. 25, 153). 2. *Barbaloïns,* which yield aloetic acid $C_{14}H_4(NO_2)_4O_2$, chrysammic acid $C_{14}H_2(NO_2)_4(OH)_2O_2$, picric and oxalic acids, and are reddened by nitric acid. *α-Barbaloïns,* from Barbados aloes reddened in the cold by strong nitric acid (Tilden, Pharm. J. [3] 2, 845; Chem. Soc. Trans. 25, 488). *β-Barbaloïns,* from Socotrine, Zanzibar, and Jafferabad aloes, coloured only on heating with ordinary, and in the cold with fuming, nitric acid (Flückiger, *l.c.*; Tilden, Chem. Soc. Trans. 28, 1270; Pharm. J. [3] 4, 208).

Barbados aloes, analysed by Tschirch and Pedersen (Arch. Pharm. 236, 200), was found to contain 12·25 p.c. *barbaloïn,* 12·65 p.c. resin, 1·75 p.c. ash, 10·5 p.c. amorphous constituents soluble in water, and 0·15 p.c. of an orange colouring matter, *aloe-emodin* $C_{15}H_{10}O_5$, m.p. 216°. Barbaloïn $C_{16}H_{18}O_7$ or $C_{16}H_{16}O_7$(?) was isolated by Smith (Chem. Gaz. 1851, 107), and first examined by Stenhouse. It consists of pale-yellow needles, which melt at 147° and readily become discoloured when moist. Leger (Compt. rend. 125, 185; 127, 234), by recrystallisation of partially purified barbaloïn from methyl alcohol, has obtained *isobarbaloïn,* isomeric with barbaloïn. *Iso*barbaloïn crystallises from methyl alcohol in efflorescent crystals with three mols. of methyl alcohol, or from water with two mols. of water of crystallisation. On fusion with caustic potash, barbaloïn yields orcin, *p*-hydroxybenzoic and aloricinic acids (Hlasiwetz, Annalen, 134, 237; 136, 31), and on oxidation with chromic acid breaks up into carbon dioxide, acetic acid, and *aloexanthin* (Tilden, Pharm. J. [3] 8, 231; Chem. Soc. Trans. 32, 264, 903). Oesterle and Babel (Chem. Zentr. 1904, ii. 340) have shown, how-ever, that Tilden's aloexanthin is a mixture of aloe-emodin and rhein, the latter compound

being identical with the rhein isolated from rhubarb by Hesse (Annalen, 309, 43).

The resin from Barbados aloes on hydrolysis gives cinnamic acid and a resin alcohol *aloresinotannol* $C_{32}H_{36}O_6$, consisting of a greyish-brown powder (Tschirch and Pedersen). By the action of alcoholic hydrogen chloride, Oesterle (Arch. Pharm. 237, 81) obtained a trihydroxy-methylanthraquinone $C_{15}H_{10}O_5$, m.p. 224°, identical with the aloe-emodin of Tschirch and Pedersen ; also Leger (Compt. rend. 134, 1111) has obtained aloe-emodin by treatment of barbaloïn or *iso*barbaloïn with sodium peroxide.

According to Leger (J. Pharm. Chim. iv. 20, 145 ; Compt. rend. 150, 983), both barbaloïn and *iso*barbaloïn left in contact with alcohol for a long time, give a pentose aloïnose. This sugar has since been shown by Leger (Compt. rend. 150, 1695) to be identical with *d-arabinose*.

The aloïn from Natal aloes has the composition $C_{24}H_{26}O_{10}$, with varying amounts of combined water. It softens at 180° and melts with decomposition at 210°. On acetylation a penta-acetyl derivative is formed. *Nataloïn* differs from barbaloïn by its resistance to alkalis, and by containing a methoxyl group (Groenwold, Arch. Pharm. [3] 28, 115). Leger (Compt. rend. 128, 1401) has isolated two aloins from Natal aloes : *nataloïn*, the compound more soluble in methyl alcohol, to which he gives the formula $C_{16}H_{18}O_7$; and *homonataloïn* $C_{15}H_{16}O_7$, the less soluble constituent. Tschirch and Klaveness (Arch. Pharm. 239, 231), however, could not detect any substance corresponding with Leger's homonataloïn.

The resin from Natal aloes when hydrolysed gives *nataloresinotannol* $C_{22}H_{18}O_4(OH)_4$, consisting of a brown powder, and *p*-coumaric acid. Nataloresinotannol gives a tetra-benzoyl derivative ; it yields oxalic and picric acids when oxidised with nitric acid, and on fusion with potash gives phloroglucinol and fatty acids.

Nataloïn, heated with sodium peroxide, yields nataloemodinmethylether, m.p. 238°, which on heating with concentrated hydrochloric acid is converted into nataloemodin, consisting of orange-red needles, melting at 220·5° (Leger).

The aloïns from Curaçao, Cape Socotra, Uganda, and Jafferabad aloes are probably identical with barbaloïn. *Zanaloïn* from Zanzibar aloes appears to be different (Leger, J. Pharm. 25, [vi.] 513 ; Tschirch and Hoffbauer, Arch. Pharm. 243, 399). The latter chemists show that Barbados aloes contain but little *iso*aloïn, Jafferabad none, whilst that from Curaçao contains a considerable proportion.

Uses.—Chiefly in medicine and as a hop-substitute. It has also been used as a source of certain dyeing materials (Ure, 1, 104 ; Preston, Chem. Zentr. 1876, 390 ; Chem. Soc. Trans. 32, 378). Kayser (Chem. Tech. Report, 1876–80) finds aloe colouring matters make certain aniline dyes faster.

Properties and Reactions.—Pure aloes is soluble in ether and almost completely soluble in water, the solution being coloured dark-brown by alkalis, black by ferric chloride, and grey by lead acetate (Flückiger). By adding a solution of copper sulphate or chloride to a solution of aloes, an intense yellow-coloured solution is obtained, which, warmed with potassium bromide or chloride, turns to a deep-red and

reddish-violet tint (Klunge, Ber. 16, 691 ; Arch. Pharm. 1883, 363). This reaction is due to *iso*-barbaloïn, for barbaloïn, recrystallised several times from methyl alcohol, does not give the test (Leger, Compt. rend. 131, 55). Bornträger (Zeitsch. anal. Chem. 19, 165 ; Ber. 13, 1040) extracts with twice the volume of benzene, and adds to the clear extract a drop of ammonia, when, on warming and shaking, the solution becomes violet-red ; Groves (Pharm. J. [3] 11, 1045) finds that this colour is not due to aloïn, but probably to a tannin-like substance. According to Tschirch and Pedersen, this test depends on the presence of aloe-emodin. Lenz (Zeitsch. anal. Chem. 21, 220) extracts with amyl alcohol, evaporates the extract, treats with nitric acid, and then with potassium cyanide and hydroxide, when a blood-red colouration is obtained. Cripps and Dymond (Pharm. J. [3] 15, 633) test for aloïn by dissolving 1 grain in 16 drops of strong sulphuric acid, then adding 4 drops of nitric acid (1·42) and 1 ounce of water, when a deep orange or crimson colour is produced, deepened by ammonia ; substances containing chrysophanic acid behave in a similar manner, but their aqueous solution turns pink upon the addition of ammonia. Aschan (Arch. Pharm. 241, 340) gives in tabular form a comparison of the reactions of the chief varieties of aloes.

For the estimation of aloïn in aloes, Schaefer (Jour. Pharm. [vi.] 5, 296) recommends the following : 50 grams of aloes are dissolved in 300 c.c. of warm water to which a few drops of hydrochloric acid have been added. When cold the solution is separated from the resin, 50 c.c. of 20 p.c. aqueous ammonia and a solution of 15 grams of calcium chloride in 30 c.c. of water are added, and the whole rapidly shaken. At the end of fifteen minutes the precipitate is separated and triturated in a mortar with hydrochloric acid. The free aloïn and the calcium chloride are dissolved in as little water as possible, filtered if necessary, and the residue washed with boiling water. The aloïn separates from the aqueous solution on cooling. A. S.

ALOES, ESSENTIAL OIL OF. A pale-yellow mobile liquid to which the odour of aloes is due. Sp.gr. 0·863, boils at 266°–271°. It exists in small quantities in aloes, and when pure has the taste and odour of peppermint (Pharm. J. [3] 10, 613).

ALOES WOOD. A name applied to the wood of *Aquillaria Agallocha* (Roxb.), a leguminous tree of Cochin China, and to that of *A. malaccensis* (Lam.) of tropical Asia. Both are highly fragrant and aromatic ; used in fumigations and pastilles, and occasionally by cabinet-makers and inlayers.

The same name is applied to the resin. Of all perfumes this is said to be the most esteemed by Orientals.

ALOIN *v.* GLUCOSIDES.

ALOO BOKHARA, ALPOGADA, PAZHAM. The Bokhara plum (*Prunus insititia* (Linn.) [*P. bokhariensis*], largely imported from Bombay. Used as a laxative. The root is astringent ; the gum is used as a substitute for gum arabic under the name of Persian gum (Dymock, Pharm. J. [3] 9, 145).

ALOUCHI RESIN *v. Aluchi resin*, art. RESIN.

ALPHOL *v.* SYNTHETIC DRUGS.

ALPINIA OFFICINARUM *v.* GALANGA ROOT.

ALPINIA OIL. An essential oil obtained from the leaves of *Alpinia malaccensis*; sp.gr. 1·02 at 26°, rot. power +6·5°. Consists mainly of methyl cinnamate, together with *d*-pinene (Van Romburgh, Proc. K. Acad. Wetensch. Amsterdam, 1900, 3, 451).

ALPININ *v.* GALANGA ROOT.

ALPOGADA *v.* ALOO BOKHARA.

ALQUIFON. Black lead ore or Potters' ore. A native lead sulphide, used by potters to glaze coarse ware.

ALSOL *v.* SYNTHETIC DRUGS.

ALSTONIA BARK. The bark of *Alstonia constricta* (F. Muell.), an apocynaceous tree growing in Australia. It has a bitter taste, slightly camphorous odour, contains a neutral bitter principle (similar to *cailcedrin* and *tulucumin*), a volatile oil smelling like camphor, an iron-greening tannin, resin, fat, wax, a protein-like substance, oxalic and citric acids (Palm, J. 1863, 615).

Müller and Rummel (Chem. Soc. Trans. 35, 31) obtained a yellow substance to which they gave the name *alstonine*. Oberlin and Schlagdenhauffen (Pharm. J. [3] 10, 1059; Chem. Soc. Abstr. 38, 127) showed that this body consisted of two compounds *alstonine* and *alstonicine*, the former being soluble in acids with fluorescence, the latter without.

Hesse subsequently (Ber. 14, 264; Annalen, 205, 360) isolated:

Alstonine (chlorogenine) $C_{20}H_{21}N_2O_4$, a brown amorphous mass, a strong base, soluble in chloroform, alcohol, and sparingly soluble in ether, and melting when anhydrous at 195° (uncorr.)

Porphyrine $C_{21}H_{25}N_3O_3$, a white powder melting at 97° (uncorr.), soluble in alcohol, chloroform, ether, and acids, with blue fluorescence.

Porphyrosine, soluble in acetic acid, forming a pink solution.

Alstonidine, colourless needles, melting at 181° (uncorr.), soluble in chloroform, ether, alcohol, and acetone.

Hesse, however, could not find a trace of quinine (Ber. 11, 1546, 1753).

ALSTONIA SPECTABILIS. *Poelé bark.* Contains *alstonamine* (Hesse, Ber. 11, 1548), and the alkaloids of dita bark. It contains six times as much echitammonium hydroxide as dita bark (Hesse, Annalen, 203, 144).

Its physiological action is like that of curare.

ALSTONITE. A rare mineral consisting of barium and calcium carbonate $(Ba,Ca)CO_3$, crystallising in the orthorhombic system. The small crystals have the form of acute six-sided pyramids, and consist of complex twin intergrowths. Found in 1834 in a lead- and zincmine near Alston in Cumberland, and in 1909 in a coal-mine near Durham.   L. J. S.

ALTI. Indian name for a root used at Goa as a substitute for Althæa (Dymock, Pharm. J. [3] 8, 101).

ALUDEL. The aludels of the earlier chemists were pear-shaped pots generally made of earthenware, but sometimes of glass, open at both ends. Each aludel had a short neck at the top and bottom, so that a series of them could be fitted together by means of the necks. The earthenware pear-shaped vessels in which the mercurial vapours are condensed at Almaden in Spain are also known as aludels.

ALUM *v.* ALUMINIUM.

ALUMINATES *v.* ALUMINIUM.

ALUMINIUM. Sym. Al. At. wt. 27·1.

Occurrence.—Aluminium is the most widely distributed element in nature with the exception of oxygen and silicon. It is not found in the metallic state.

As oxide, Al_2O_3, aluminium is found in *corundum*, or, coloured by metallic oxides, in *sapphire*, *ruby*, *emery*, &c. The hydrated oxide Al_2O_3,H_2O occurs as *diaspore*, and, together with ferric oxide, silica, &c., as the important mineral *bauxite*.

Aluminium occurs in combination with oxygen and metals as *aluminates*, in *spinel* $Al_2O_3.MgO$, *chrysoberyl* $Al_2O_3.BeO$, *gahnite* $Al_2O_3.ZnO$. As hydrated sulphate it is found in *aluminite* or *websterite* $Al_2O_3SO_3,9H_2O$, and as *alunogen* $Al_2O_3(SO_3)_3,18H_2O$; as the double sulphate of aluminium and potassium in *alumstone* or *alunite*; and, as an efflorescence on aluminous minerals in the form of the alums of potassium, sodium, ammonium, &c.

Aluminium occurs principally, however, as silicate in the various *clays*; as silicate containing silicon fluoride in the *topaz*; and, as double silicate, with iron, magnesia, lime, &c., in *garnets*; with potassium, sodium, magnesium, and calcium in immense quantities in the varieties of *felspar*.

As double fluoride of aluminium and sodium it is found in *cryolite* $Al_2F_6.6NaF$; as hydrated phosphate in the *turquoise* and in *wavellite*, and as borate in a crystalline mineral occurring in Siberia.

Although present in such quantities in the soil, aluminium is not usually considered a constituent of the ash of plants except of cryptogams; Yoshida, however (Chem. Soc. Trans. 1887, 748), has found it in a number of phanerogams in Japan.

History.—The name of this metal is derived from *alumen*, a term applied by the Romans to all bodies of an astringent taste. Pott, in 1746, stated that the basis of alum is an argillaceous earth; and in 1754 Marggraf pointed out the distinction between alumina and lime, and its presence in combination with silica in clay.

Davy, in 1807, having isolated the alkali metals by electricity, endeavoured, unsuccessfully, to reduce alumina in the same manner.

Oersted, in 1824, prepared aluminium chloride by passing chlorine over a mixture of alumina and carbon heated to redness. He appears to have reduced the chloride to the metallic condition by heating with potassium amalgam: (Berzelius, Jahresb. 1827,[6]118). The amalgam produced oxidised rapidly in the air, and left, on volatilising the potassium, a tin-white metal.

Wöhler, in 1827 (Annalen, 1828, 37, 66), having failed to procure the metal by Oersted's method, obtained it by the decomposition of the *anhydrous* chloride with potassium, as a grey powder, which became brilliant under the burnisher.

Bunsen and Deville, in 1854, independently, obtained the metal by electrolysis of the fused chloride. Deville, in the same year, much simplified the manufacture by substituting sodium for the more expensive potassium. In 1854 he was installed in the manufactory of Javel by the Emperor Napoleon III., and supplied with the necessary apparatus for experiments

on the large scale. Afterwards his process was removed to Nanterre and finally to Salindres. A description of his method is given in Ann. Chem. Phys. [3] 43, 5–36, and specimens of the metal produced were shown at the Paris Exhibition of 1855.

Shortly after the publication of these results, Messrs. Dick and Smith, under the direction of Dr. Percy, prepared aluminium by the action of sodium on the then newly discovered mineral *cryolite*, some of the product being shown by Faraday at the Royal Institution in March, 1855 (Phil. Mag. 10, 365).

About six months subsequently, Rose, independently, prepared it in the same manner, and published his results in an extended article in P. 96, 152 (Phil. Mag. 10, 233).

Deville at once turned his attention to this process (Ann. Chim. Phys. [3] 46, 451); but on account of the impurity of the metal produced, he preferred the double chloride of aluminium and sodium, using cryolite as a flux only.

The first manufactory in England was started at Battersea, London, in 1859, by F. W. Gerherd. Some of his metal was shown at the Society of Arts Exhibition in 1860. Messrs. Bell, of Newcastle, also prepared aluminium and aluminium bronze in 1863, using Netto's process. A mixture of 200 lbs. of cryolite and an equal weight of common salt was brought to fusion, and 40 lbs. of sodium gradually added. The charge thus contained only 5 p.c. of aluminium, but less than half of this was obtained in the yield.

The manufacture ceased in 1874. In Grabau's process (J. Soc. Chem. Ind. 1891, 433) aluminium fluoride was subjected to the action of metallic sodium. Other modifications were proposed from time to time, but the production of aluminium made no notable advance. Weldon, in 1883, summed up the position of the industry in the statement that 'the only method known for the manufacture of aluminium is Deville's. M. Pechiney has improved and cheapened the modes of working, and the appliances for carrying that method into effect, but this is all the progress which has been made in the manufacture of aluminium during the last five and twenty years.'

When the great stability of the available compounds containing aluminium is considered, it is not to be wondered at that the many attempts that have been made to prepare the metal by the action of the usual reducing agents, such as carbon, hydrogen, or hydrocarbons, have met with so little success. The heat of formation of these compounds is an index to their stability, and may be taken as a measure of the energy requisite for the isolation of the aluminium. The operation is not likely to succeed unless the elements which become separated from the aluminium enter into new combinations of still greater stability. The nature of the changes that might be expected to take place may be expressed in the following equations :—

$$2Al_2O_3 + 3C \qquad 4Al + 3CO_2$$
$$Al_2O_3 + 3C \qquad 2Al + 3CO$$
$$Al_2O_3 + 6H \qquad 2Al + 3H_2O$$
$$Al_2O_3 + 6Na \qquad 2Al + 3Na_2O$$
$$Al_2Cl_6 + 6H \qquad 2Al + 6HCl$$
$$Al_2Cl_6 + 6Na \qquad 2Al + 6NaCl$$
$$Al_2F_6 + 6Na \qquad 2Al + 6NaF.$$
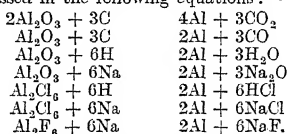
In order that there may be a likelihood of these reactions occurring, the heat arising from the formation of the compounds on the right hand should exceed the heat concerned in the decomposition of the aluminium compounds on the left. The following table will show how far this is the case :—

	Calories		For amount equivalent to 2Al
Al_2O_3	391,600	$\frac{3}{4}CO_2$	145,500
		$3CO$	86,400
		$3H_2O$	174,900
		$3Na_2O$	302,700
Al_2Cl_6	323,600	$6HCl$	132,000
		$6NaCl$	587,400
Al_2F_6	558,000	$6NaF$	604,200

It will be seen that only the last two reactions will be at all likely to take place, and these heat values indicate that sodium is a much more favourable reagent than carbon or hydrogen, and that the highest excess of heat evolved over that absorbed occurs in the case of the aluminium chloride in presence of sodium.

The following analyses, taken from Hoffmann's Ber. Entwick. Chem. Ind. (1) 603, show the composition of commercial aluminium as produced under Deville's process :—

	1	2	3	4	5	6	7	8	9	10
Locality	Paris	Paris	Berlin	Paris	Paris	Paris	Bonn	Nanterre (Morin)		
Analyst	Salvétat	Salvétat	Mallet	—	Dumas	Dumas	Kraut	Kraut	Kraut	Sauerwein
Aluminium	88·35	92·97	96·25	92·60	92·5	96·16	94·7	—	—	97·2
Silicon	2·87	2·15	0·45	0·45	0·7	0·47	3·7	0·04	0·12	0·25
Iron	2·40	4·88	3·29	7·55	6·8	3·37	1·6	1·62	2·26	2·40
Copper	6·38	—	—	—	—	—	—	—	—	—
Lead	trace	—	—	—	—	—	—	—	—	trace
Sodium	—	trace	trace	—	—	—	—	—	—	—

Moissan has shown (Compt. rend. 121, 851) that it contained also from 0·1 to 0·5 p.c. of sodium ; 0·3 to 0·4 p.c. of carbon and other impurities. These impurities would have a very considerable effect on the properties of the metal, and any statements based on observations with such metal, or even with the metal now being made, must be accepted with caution.

The production even in 1885 was small and did not exceed $2\frac{1}{2}$ tons at Salindres and $2\frac{1}{2}$ cwt. in the United States.

According to Mallet, pure aluminium may

be prepared by the method adopted by him in his determination of the atomic weight of that element (Phil. Trans. 171, 1018). Ordinary commercial aluminium is converted into bromide by the direct action of bromine. On account of the violence of the action, the metal should be immersed only for a short time, at intervals, until dissolved, or should be added in very small pieces. The bromide so produced is freed from bromine by distillation and fractionally distilled, that portion boiling uniformly at 263·3° being reserved. This portion is colourless, entirely soluble in water, and consists of the pure bromide.

It is heated with sodium (which has been carefully freed from oil and well scraped) in a crucible made of a mixture of pure alumina and sodium aluminate. The amount of sodium used should not be sufficient to reduce the whole of the bromide, or the aluminium is liable to contain sodium. The globules of metal are fused together before the blowpipe on a bed of alumina, immersed for a short time in hydrochloric acid, washed and dried. Pure aluminium might also be produced by the electrolysis of the pure bromide or chloride.

The purification from metallic impurities on the large scale involves many difficulties. The only method of obtaining satisfactory metal is to ensure as high a state of purity as possible in the first instance by making use of selected materials and avoiding contamination in the process of manufacture.

By the establishment of Deville's process the price of aluminium had been brought down from 18*l*. per lb. to 1*l*., at which it stood till 1887.

The double chloride of sodium and aluminium used contained only 14 p.c. of aluminium, and the working of large charges with a small yield together with the high cost of sodium and fuel stood in the way of any prospect of reduction in the price of the metal.

The introduction of Castner's process, by which sodium could be produced much more cheaply, led to the establishment of the Aluminium Company's works at Oldbury, and effected some reduction in the price of aluminium. Meanwhile Messrs. Cowles (Patents Aug. 18, 1885, and Jan. 26, 1886) brought electrical heating into operation, and, though their process was not adapted to the production of aluminium, it was capable of furnishing alloys of aluminium with copper and other metals. These could be made at one-tenth the price which had ruled for aluminium, and the valuable properties of aluminium bronze, Hercules metal, and other alloys were soon recognised. Moreover, the discovery of the effect of the addition of minute amounts of aluminium to iron and steel gave a further stimulus to the production of aluminium. C. W. Siemens had already described an electric furnace (1881) capable of giving very high temperatures, and the type of furnace patented by Messrs Cowles Bros. was based on similar lines.

The furnace is a rectangular box, one foot wide, five feet long, and fifteen inches deep, all inside measures. Two carbon electrodes pass through pipes in the ends ; they are three inches in diameter and thirty inches long ; this size could not be exceeded, as larger carbons dis-

integrated under the intense heat. For a non-conducting furnace lining, fine particles of charcoal are washed in lime-water, exposed to the air and dried. They thus become coated with lime and are of good insulating power. At the high temperature produced, ordinary charcoal becomes converted into graphite and forms a good conductor. The two electrodes being within a few inches of one another, the charge of twenty-five parts of corundum, twelve parts of carbon, and fifty parts of granulated copper is placed around and between them, covered with small lumps of charcoal, and the whole covered with an iron top lined with firebrick. The current from a powerful dynamo is then passed, and the electrodes moved if necessary to produce the requisite resistance. In about ten minutes, the copper having melted between the electrodes, the distance between them is increased while the current is raised to 300 amperes of fifty volts E.M.F. and the yield 1 lb. per E.P.H. hour. As the resistance is increased, the temperature rises, the alumina is reduced to the metallic condition and alloys with the copper, while its oxygen forms carbon monoxide and burns at the openings in the cover with a white flame. After about five hours the operation is completed. The alloy produced is brittle, consisting of copper and 15 p.c. or upwards of aluminium. When boron or silicon oxides have been added, the bronzes produced contain these elements. It is melted, cast into ingots, the percentage of aluminium determined, and sufficient copper added to produce 'aluminium bronze,' or the required alloy.

When other metals, such as iron, nickel, silver, &c., are substituted for copper, corresponding alloys are produced.

The slag produced is hard and compact, but soon falls to a fine alkaline powder ; it contains alumina, calcium aluminate, with traces of copper, silicon, &c.

Pure aluminium cannot be produced satisfactorily by this method, as it remains, to a great extent, mingled with the carbon.

See further, W. P. Thompson (J. Soc. Chem. Ind. 1886, 206) ; Mabery (Amer. J. Sci. 308, and Amer. Chem. J. 1887, 11).

The Electrical Process.—A new principle was, however, introduced into metallurgy, and the application of electricity for purposes of heating and reduction of metals has made rapid progress in recent years. Its full development had not, however, been reached in the process just described. It had been shown that, though the fusion of a substance like alumina could not be economically effected owing to its high resistance, the addition of copper and other metals enabled the furnace charge to conduct the current. If a suitable solvent could be found for alumina then the electrolytic action of the current could be brought into play. When this was accomplished the chemical method of decomposition would give place to the electrolytic method, and the isolation of aluminium become a question of a sufficient current at the necessary voltage. This voltage can readily be calculated from the heat of formation of the compound in question by dividing the number of calories per equivalent by 23,250. We thus obtain for alumina 2·81 volts, for

aluminium chloride 2·32 volts, for aluminium fluoride 4·00 volts, for aluminium sulphide 0·9 volt.

A suitable solvent is found in native cryolite $3NaF·AlF_3$, which may be brought to fusion below 1000°, and will dissolve 15 to 20 p.c. of its weight of alumina, and in this condition it is likely that the voltage is somewhat lower—in the case of alumina about 2·3 volts.

In the year 1886 the Héroult process was patented and soon came into use at Neuhausen, and at the Société Electrométallurgique at Froges, near Grenoble. In this process the anodes consisted of carbon and the cathode was the carbon lining of the furnace, the distance between the anode and cathode being capable of adjustment by raising or lowering the anode. The cryolite was first melted in the bath by utilising the heat generated by the resistance to the electric current, and then alumina was added, and the additions continued from time to time as the bath became exhausted. The metallic aluminium settled at the bottom of the bath in the neighbourhood of the cathode, and was tapped every 24 hours.

The purity of the metal at first was 97-99 p.c. There were at disposal 360 kilowatts at Froges, and just over 1000 kilowatts at Neuhausen (J. Soc. Chem. Ind. 1892, 910); the yield usually obtained was about $1\frac{1}{2}$ lbs. of aluminium per kilowatt-day, an efficiency of less than 25 p.c.

The Hall process, brought out in the United States about the same time, only differed from Héroult's in matters of detail, the anodes being rods of carbon 3 inches in diameter, or of larger dimensions banded together, the electrolyte being alumina dissolved in mixed fluorides of calcium and aluminium or $AlF_3·NaF$.

Minet (Compt. rend. 112, 231) used a bath composed of 62·5 p.c. of common salt and 37·5 p.c. of cryolite, but his metal seems to have contained 2 to 3 p.c. of impurity, which was chiefly silicon, owing largely to the impurity of the alumina used by him. Aluminium so prepared was liable to contain sodium, owing to the fact that the voltage necessary for the decomposition of aluminium fluoride differed so little from that required to decompose sodium fluoride—viz. 4·7 as against 4.

There was added to the bath as the operation proceeded, a mixture of hydrated alumina, cryolite, and alumina dissolved in cryolite.

Kleiner invented a furnace for the decomposition of cryolite, and carried on the production of aluminium at Tyldesley in Lancashire; a plant was also operated on the lines of the Héroult system at Patricroft near Manchester.

In this case the dynamos were run by steam power, and it soon became manifest that this could not compete with advantageous supplies of water power which began to be called into requisition wherever such power was available.

Mention should also be made of the method of Bucherer, D. R. P. 63995 (1892), who prepared aluminium by electrolysing the double sulphide of aluminium and an alkali or alkaline earth, the chief obstacle to success being the expense and difficulty attending the production of the sulphide.

It soon became evident that the Hall and Héroult process must hold the field, and that

coal could not compete with cheap water power in this industry, and rapid expansions of the industry were made. The price had by 1891 been brought down to one-fifth of that which had ruled under Deville's process, and the production had increased to over 300 tons per annum. The accompanying statement is the cost of production at this period, as given by A. E. Hunt (Eng. and Mining Journ. 1891, 280). For 1 lb. of aluminium there was requisite

2 lbs. alumina	costing 6 cents	
1 lb. carbon electrode	,, 2	,,
Chemicals, pots, &c.	,, 1	,,
22 E.H.P one hour	,, 5	,,
Labour, interest, repairs	,, 5	,,

making 19 cents in all.

The following firms were at this period manufacturing either aluminium or its alloys:—

In England—
    Cowles Syndicate (Cowles process).
    Reduction Syndicate (Hall process).
In the United States—
    Pittsburg Reduction Company.
    Cowles Electric Smelting Company.
    United States Aluminium Metal Co.
On the Continent—
    Société Electrométallurgique at Froges.
    Aluminium Industrie Actien-Gesellschaft at Neuhausen.

Further progress was mainly in the direction of increasing the yield and bringing down the cost of production whilst perfecting the various details of the process so that a purer product could be made.

We shall now describe the further development of the industry and the manufacture as it stands to-day after over 20 years of experience; and in doing so it will be well to consider in greater detail (a) the production of alumina, (b) the making of the carbon electrodes, (c) the nature and arrangement of plant, including the reduction furnaces.

Development of the Aluminium Industry.— The first factory established on electrical lines was that started in 1888, at New Kensington, by the Pittsburg Company, which is now known as the Aluminium Company of America, and conducts operations at the Niagara Falls, the Shawingian Falls, and at Massena.

Amongst the pioneers of the industry were also (1) Aluminium Industrie Aktien-Gesellschaft, who control works at Neuhausen, Rheinfelden, and Lend Gastein; (2) the British Aluminium Company, with reduction works operating in 1896 at Foyers and now at Kinlochleven (Argyllshire), and branch works at Greenock, Larne, and Milton (Staffordshire),—this company is also associated with reduction works at Stangfiord (Norway), and projected works at Orsières (Switzerland); (3) Société Electrométallurgique Française at Froges, La Praz, and St. Michael, and the Cie. des Produits Chimiques d'Alais et de la Carmargue.

There are also works on a smaller scale under the Aluminium Corporation at Wallsend, with construction going on at Dolgarrog (N. Wales), the Anglo-Norwegian Company at Vigeland Falls (Norway), and developments in Italy at Bussi. The cost of production of the metal to-day is said to be 61l. per ton as a minimum, though at most works it would reach 80l. (Mining World, June 26, 1909).

The market price of aluminium ingots in 1902–4 was 120l. per ton, but it rose to 200l. in 1906, and has since then fallen to 65l. (1909), though it is now again advancing. Since 1902 no trustworthy record has been made of the world's output of aluminium. It remained, however, fairly stationary in the neighbourhood of 8000 tons from 1900 to 1905 inclusive, and since then has grown steadily, and may be estimated for 1909 at 30,000 tons. In the United States Geological Survey publications (Metallic Products) for 1908 there may be found the estimated consumption of metal in the United States, from which it appears that in 1907 this amounted to nearly 7700 tons, and in 1908 to nearly 5000 tons.

The following is a statement of the production of aluminium in metric tons from 1889 to 1899, (a) in the United States, (b) total output :—

		a		b
1889	.	22	.	93
1890	.	28	.	193
1891	.	68	.	302
1892	.	118	.	505

		a		b
1893	.	154	.	870
1894	.	250	.	1491
1895	.	417	.	1835
1896	.	591	.	2250
1897	.	1814	.	5220
1898	.	2359	.	6860
1899	.	2948	.	8950

The Production of Alumina.—The raw material from which the alumina is usually made is bauxite, deposits of which occur at Beaux and in the Var (S. France), at Feistritz (Austria), Wochein (Styria), Irish Hill (Ireland), Georgia, Arkansas, Alabama (United States), and in New South Wales. The physical condition of the bauxite varies considerably, so that some kinds are more readily acted upon for the production of alumina than others. In the aluminium industry a low content of iron and silica is desired, especially the latter ; it is therefore usually found advantageous to employ the red bauxites, the white bauxites being used preferably in the manufacture of sulphate of alumina. The following table gives the composition of typical samples :—

Locality	Beaux		Var		Wochein		Feistritz			Irish	Georgia
			Red	White	Dark coloured	Light coloured	Reddish brown	Yellow	White	Raw	
Al_2O_3	60	75	50–62	65–74	63·16	72·87	44·4	54·1	64·6	35·0	60·5
Fe_2O_3	25	12	24–28	0·3–3	23·55	13·49	30·3	10·4	2·0	38·0	1·9
SiO_2	3	1	1–7	12–18	4·15	4·25	15·0	12·0	7·5	3·5	3·3
H_2O	12	12	12–13	14	8·34	8·50	9·7	21·9	24·7	21·5	32·1
TiO_2	—	—	0·1–4	—	trace	trace	—	—	—	2·0	2·2

The following analyses by Leop. Mayer and O. Wagner (Dingl. poly. J. 248, 213) show that the appearance of bauxite cannot be relied on as a criterion of its value. The origin of the samples is not given :—

	Appearance		Hygroscopic moisture	Combined water	Al_2O_3	Fe_2O_3	SiO_2	MnO_2	CaO	MgO	P_2O_5
1	Pure white	.	2·33	13·86	29·80	3·67	44·76	—	2·75	0·84	1·47
2	Yellow .	.	1·03	27·85	43·22	14·39	10·43	—	1·61	—	1·13
3	,, .	.	1·30	27·70	50·38	11·68	8·34	trace	trace	trace	0·61
4	Red .	.	1·34	23·12	33·86	25·69	12·41	2·42	trace	—	0·53
5	,, .	.	1·31	23·81	46·18	22·05	4·82	—	0·89	—	0·66
6	,, .	.	0·95	20·83	62·10	6·11	5·06	2·01	3·20	trace	trace
7	,, .	.	1·17	4·75	21·80	3·75	60·10	—	6·06	2·49	trace

The amount of bauxite mined in 1907 was 260,000 tons, three-fifths of which was produced in France.

For the manufacture of the purest form of alumina the bauxite is first roughly powdered and calcined to get rid of water and any organic matter. It is then more finely ground and introduced gradually with agitation into kiers containing caustic soda solution of 1·45 sp.gr. The kiers are now closed and the charge heated for some hours under high-pressure steam—about 70–80 lbs. The contents of the kiers are then transferred to the filter presses, and the filtrate further cleared through wood pulp in lead-lined vats. The liquor contains essentially sodium aluminate, which may be decomposed by passing carbon dioxide into it, but it is now more usual to adopt the Bayer method of precipitating the alumina.

This method depends on the fact that the addition of alumina effects the decomposition of the aluminate and throws down some 70 p.c. of the alumina. The dissolved liquor now contains alumina and soda in the proportion $Al_2O_3 : Na_2O :: 1 : 6$. The precipitated hydrate of alumina is allowed to settle, and the liquor with its undecomposed portion is run off into weak-liquor tanks. The hydrate is filter-pressed, sufficient being left in the vat to serve as precipitant for the next charge. The weak liquor may, after concentration, be used over again for reacting upon a further amount of bauxite.

The hydrate of alumina so obtained ought to contain less than 1 p.c. of mineral impurity, sodium and silicon being the more objectionable impurities. To bring it into a suitable physical

condition for use in the reduction furnaces it must be calcined at 1100°–1200°, so that it shows no tendency to give up moisture when used in the furnace or to absorb moisture when exposed to air.

The alumina of to-day is superior to that of fifteen years ago, and the cost of production less than one-half. It constitutes, however, about one-fifth of the whole cost of manufacture of aluminium, and many processes have been brought forward with a view to improve or cheapen the product. Of these may be mentioned the patents of Penokoff (Erg. Pat. Nov. 19, 1895, Mar. 18 and May 13, 1896, &c.). Endeavours have been made to obtain alumina of sufficient purity from bauxite, clay, felspar, or kaolin by electrically heating them with iron (or its oxide), carbon and cryolite, thus separating ferrosilicon from alumina; Moldenhauer (J. Soc. Chem. Ind. 1909, 148), Sinding-Larsen (*ibid.* 1908, 409), and Tone (Electrochem. and Metallurg. Ind. 1909, 35), Hall (J. Soc. Chem. Ind. 1902, 49). Recently Serpek has proposed to prepare alumina by forming the carbide and acting upon this with producer gas consisting of 77 p.c. nitrogen, 23 p.c. carbon monoxide, and a little carbon dioxide. He claims that a tolerably pure nitride of aluminium is formed, and this decomposed by steam yields alumina and ammonia (Journal du Four Electrique, 315, 1; J. Soc. Chem. Ind. 1911, 26; Fr. Pat. 405712 and 418059).

The Making of Carbon Electrodes.—Bituminous coal, anthracite, retort carbon, natural or artificial graphites, soot and oil-coke are all materials which have from time to time been used in the production of carbon electrodes. In deciding which of these materials should be used, account must be taken of: (*a*) Supply and cost of raw material; (*b*) ash content; (*c*) amount of volatile matter and sulphur; (*d*) conductivity for electricity and heat. It must also be understood that electrodes used for the production of aluminium differ in character from those used for lighting or for the production of calcium carbide and many other purposes where graphitisation of the carbon is an advantage and the presence of mineral matter is quite permissible and even necessary. The graphitisation of amorphous carbon is indeed effected by exposing it to a high temperature under electrical heating after admixture with finely divided iron.

It is said that at the temperature employed the iron volatilises. Be this as it may, the ash of such carbon contains a considerable amount of oxide of iron. Aluminium, boron, silicon, and other elements which form carbides can be used as graphitising agents, as also to some extent the oxides of these elements.

It may be taken that, so far as it is capable of reduction in the aluminium furnace, the mineral ash contained in the carbon alloys itself with the aluminium, as also the foreign matter present in the alumina. The amount of alumina used should be about double that of the aluminium resulting therefrom, and the electrode consumption about two-thirds of the aluminium, so that an estimate may be made of the impurity as silicon contained in the metal. Assuming the silica in the alumina and in the electrode as 0·3 p.c., in each case, the

amount of silicon in the metal will be that contained in 0·8 p.c. of silica, *i.e.* 0·37 p.c.

The electrical resistance is in microhms per cubic inch of

	0°	1000°
Amorphous carbon (pressed)	1·63	1·45
Graphitic carbon	0·42	0·25
Electrodes for aluminium	3·00	2·60

The resistance per cubic centimetre would be 2·54 times these values. (For further detail, The Electric Furnace, Stansfield, or the pamphlet issued by the Acheson Graphite Co., may be consulted.) In addition to low resistance to the electrical current, it is desirable that electrodes should be of low conductivity for heat, that they should be sufficiently hard and resistant to superficial oxidation, of low porosity and of even character throughout their whole mass.

To produce electrodes having these qualities the material (oil-coke is largely used) must be carefully selected, ground, calcined, and subjected to high pressure with the admixture of tar or other material to act as binder. They are then baked at a temperature of about 1200°. in a kiln, in principle resembling a pottery kiln, the surface of the blocks being protected from oxidation by being embedded in carbon. The permissible current-density for good electrodes of this type is 25 to 60 amperes per square inch of transverse section, though in practice a much lower current-density is employed. For further details and description of Mendheim and other kilns suitable for baking the blocks, reference may be made to Die Künstlichen Kohlen, by Julius Zellner. The connection of the carbon blocks with the anode beam carrying the current may be effected by means of an iron claw let into the block or a copper hanger fitted into it by a screw contact.

The Reduction Furnaces.—These consist essentially of an iron casing lined with carbon, the general character and arrangement of which is shown in transverse section (p. 108). The electrodes vary in size and form in different works, and are not necessarily arranged in two rows as indicated in the figure. Their total sectional area is, however, always adapted to the current to be used and good electrodes will act satisfactorily under a current-density of 8 to 10 amperes to the square inch. The lower part of the carbon body serves as the cathode, and a special form of cathode is let into the carbon at the base of the furnace. In starting a furnace it is usual to introduce first the cryolite, which is brought to a state of fusion by electrical heating. Alumina is then fed in gradually at the surface of the cryolite, and as it dissolves the resistance gradually falls to about 5 or 6 volts, and the temperature of the bath will be generally 1000°. The electrolytic action brings about a decomposition, which has been usually taken to result in the formation of carbon monoxide, according to the equation

$$Al_2O_3 + 3C = 2Al + 3CO,$$
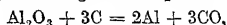
but there is little doubt that primarily carbon dioxide is formed, and the change should be expressed as

$$2Al_2O_3 + 3C = 4Al + 3CO_2.$$
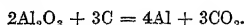
In the former case the carbon used would be two-thirds of the weight of the aluminium

produced, whilst in the latter it would be one-third. In practice the ratio of carbon to aluminium lies between these extremes.
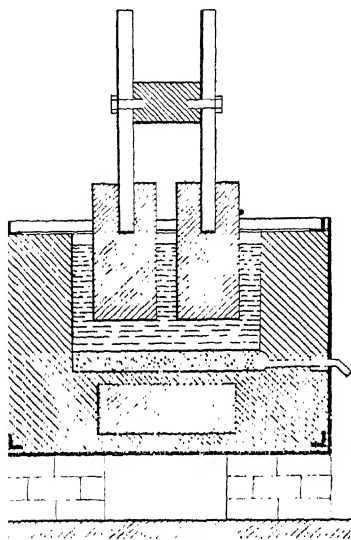
The production of aluminium is discontinuous, for about 2 hours after the proper charge of alumina has been added the voltage of the furnace rises rapidly and affords an indication that more alumina must be added. The aluminium collects at the bottom of the bath of electrolyte, and is tapped off at stated periods, either every day or at longer intervals. The reduction of alumina by electrolytic methods on a laboratory scale is beset with difficulties; an account of experiences in this direction is given in papers by Neumann and Olsen (Met. and Chem. Engineering, 1910, 185), and Tucker (*ibid.* 1909, 315).

Physical Properties.—Commercial aluminium is a metal with the whiteness of tin. It has been obtained in crystals resembling octahedra, and is very slightly magnetic.

Its specific heat is, at

$-100°$	0·1893	300°	0·2434
0°	0·2098	500°	0·2739
100°	0·2236	650°	0·3200

(Schmitz, Proc. Roy. Soc. 72,177).

The total heat required to bring a kilogramme of aluminium from 0° to 625° is 239,400 cals., and its latent heat of fusion is 80. It melts at 654·5° (Heycock and Neville), 657·3° (Holborn and Day), the melting-point being dependent (as are other physical properties) on its purity. Small amounts of silicon and iron, which are always present, have a considerable effect on its behaviour, both physically and in contact with reagents. Lorenz found its conductivity for heat at 0° 0·3435, at 100° 0·3619; whilst Jaeger and Dresselhorst for metal containing 0·5 p.c. iron and 0·4 p.c. copper, found 0·4923 at 100°. Similarly the electrical

conductivity of aluminium, taking copper as 100, is as follows : 98·5 p.c. purity, 55 ; 99 p.c., 59 ; 99·5 p.c., 61 ; 100 p.c., 66.

A sample of metal produced in 1856, having a lower degree of purity, gave 51·3.

Its elasticity modulus (*i.e.* load in kilogrammes per square millimetre, divided by its alteration in length) is 7462 as compared with 11,350 for copper, and the torsion moduli of these metals are 3350 and 4450 respectively.

The specific gravity of the molten metal is 2·54, and of the cast metal is about 2·66 ; this may be increased by rolling. Its expansion coefficient is 0·00002313 at 40° (Fizeau), and 0·0000315 at 600°. It expands on fusion to the extent of 4·8 p.c. (Toepler). In hardness it resembles silver, and the pure metal is softer than the impure. It becomes more elastic and also harder by hammering and rolling, and is capable of being drawn down to a wire of $\frac{1}{815}$ inch in thickness, or rolled into plate or beaten into foil to $\frac{1}{40000}$ inch thick. It can also be finely granulated for use in explosives, or prepared in the form of very fine powder, which is largely employed as 'thermite,' or as aluminium paint. The tensile strength of aluminium is 12 to 13 tons on the square inch, but this varies with the temper of the metal between $6\frac{1}{4}$ and $15\frac{1}{2}$ tons on the square inch, the elongation varying in the inverse manner from 23 p.c. to $1\frac{1}{2}$ p.c. Aluminium has been largely used for overhead electrical transmission and it possesses many advantages for such purposes owing to its lightness. Its specific gravity being only $\frac{1}{3}$ of that of copper, and conductivity over 60 p.c., it follows that an aluminium cable has double the efficiency of a copper cable of the same weight as a means of conveying current. The tensile strength of aluminium is affected, of course, by its form, method of casting and mechanical treatment. Its ultimate strength in tons per square inch is in castings 7 tons, in sheet 11 tons, and in wire from 13 to 29 tons.

Although corroded in the atmosphere of some large towns, it is not more so than other metals used for cables, and under ordinary circumstances it merely becomes coated with a thin film of oxide which acts protectively.

There has been great difficulty in finding a wholly satisfactory solder for the metal, and one that shall resist corrosion. Dagger (J. Chem. Soc. Ind. 1891, 436) quotes as useful for heavy soldering Al 12 pts. Cu 8 pts. Zn 80 pts., and for light soldering Al 6 pts. Cu 4 pts. Zn 90 pts. Joints can, however, be made by autogenous welding with an oxyhydrogen or acetylene flame or electrically. Butt and other joints may be effected by various mechanical devices with the aid of fusion at the surfaces or by a casting of metal around the junctions.

Chemical Properties.—Aluminium absorbs about its own volume of hydrogen, which is, however, expelled on heating or *in vacuo*. It is practically unacted upon by oxygen at ordinary temperatures, but if finely divided it undergoes considerable oxidation at 400°, or even, though less rapidly, at lower temperatures. If of sufficient purity, water has no action upon it, though when sodium is present in the metal a slight action occurs. This is accentuated if copper, brass, or other metals are in contact with it. A recent use to which the metal has

been put is for the treatment of hard waters, which by intimate contact with the metal, are said to be softened and become less liable to form incrustation on the shell of the boiler. The halogen elements or acids readily act upon aluminium, and the chemical activity of the metal is such that a large amount of heat is generated on combination with these elements. The heat of formation of Al_2O_3 is 391,600 cals., Al_2S_3 is 124,400 cals., Al_2F_6 is 558,000 cals., Al_2Cl_6 is 323,600 cals., Al_2Br_6 is 243,900 cals., Al_2I_6 is 140,600 cals.

The very great affinity which aluminium possesses for oxygen has been made use of in the application of 'thermite' as a means of reducing oxides. Goldschmidt, D. R. P. 96317 (1895), has thus used the finely divided metal in the production of iron, manganese, chromium, nickel, cobalt, titanium, boron, molybdenum, tungsten, vanadium, and other metals.

Reagents which readily part with the halogens, such as $SiCl_4$ and PCl_3, also attack it, and carbon or the oxides of carbon at high temperatures convert it into carbide, Al_4C_3. Concentrated nitric acid has very little action upon it unless the metal is impure, but more dilute acid dissolves it appreciably. Sulphuric acid only reacts if hot and concentrated, and in these circumstances there is a considerable evolution of sulphur dioxide. Alkalis or the hydroxides of the alkaline earths, especially baryta, attack the metal, and hence vessels used for culinary purposes will be corroded if brought into contact with soda. Mallet (Chem. Soc. Trans. 1876, 340) found that molten aluminium is acted upon by nitrogen with the formation of nitride.

If brought into intimate contact with mercury in presence of moisture, aluminium is readily converted into the hydroxide, and when exposed to the vapour of mercury with access of air, it undergoes rapid oxidation.

The action of organic acids on aluminium is inconsiderable. In presence, however, of sodium chloride these acids have a slight solvent action. Under like circumstances, tin and copper would be much more affected, with the production of injurious salts; the salts of aluminium are, however, quite harmless, and are almost entirely precipitated and rendered insoluble on boiling.

Perspiration, being acid, has no apparent effect; saliva, on account of its slight alkalinity, acts very slowly. Aluminium tubes have been used for insertion in the human body where much purulent matter was present, without perceptible corrosion.

Aluminium when fused with potash or soda is unaffected even at a dull red heat, but the superficial silicon is removed; metal so treated takes a good 'matt.'

Dry ammonia gas has no action; solution of ammonia has a slight action upon the metal, converting it into hydrate, whilst a portion passes into solution.

Pure aluminium is less acted upon by most reagents than the commercial metal (Mallet).

For burnishing and engraving aluminium, the ordinary media are unsuitable. According to Mourey and others, an emulsion of equal parts of rum and olive oil is most satisfactory. The finish of manufactured articles is improved by a frosted appearance. This is produced by plunging the article momentarily into caustic alkali, washing well, and immersing in dilute nitric acid.

Action on metallic solutions.—Aluminium, especially in the form of foil, has a considerable action on many salts in solution. The action of sulphates and nitrates is usually very slow. All chlorides, except those of the alkalis and alkaline earths, are readily decomposed, even *aluminium chloride* solution dissolves the metal with evolution of hydrogen. Bromides and iodides have corresponding effects. The presence of chlorides in solutions of other salts much facilitates their action.

From a neutral or feebly acid solution of silver nitrate, silver is precipitated slowly; from an ammoniacal solution of the chloride, silver is rapidly precipitated as a crystalline powder.

From the nitrate or sulphate of copper, precipitation is slow, from the acetate quicker, and from the chloride or other salt in presence of sodium chloride, rapid and complete.

Mercurous salts are decomposed with formation of an amalgam. Lead and zinc are readily precipitated (*v.* also Cossa, Zeitsch. f. Chem. [2] 6, 380 and 443).

Action of dry salts and oxides.—The action of aluminium, when heated with certain salts and oxides, is peculiar, and shows, especially at high temperatures, the tendency of this metal to form aluminates.

It is not affected by potassium nitrate except above a red heat; it is then rapidly oxidised with formation of potassium aluminate. With alkaline carbonates combination takes place at a red heat with separation of carbon, and with alkaline sulphate combination takes place suddenly at redness with explosive violence; in both cases aluminates are formed.

When finely divided aluminium is mixed with oxide of copper, lead, or iron, combination takes place at a *white* heat only, with such violence as frequently to shatter the crucible. In the case of lead and copper oxides, aluminates are produced, and with iron an alloy of iron and aluminium (Tissier).

When heated with silicates or borates, aluminium liberates silicon or boron, forming an aluminate with the base. Fused silver chloride is reduced to metal; zinc is reduced from its fused chloride, whilst magnesium chloride is not affected (Flavitzky, Ber. 6, 195). The vapour of mercuric chloride is reduced with such energy by heated aluminium that the metal fuses.

Detection.—Compounds of aluminium, when heated, moistened with solution of cobalt nitrate, and again strongly heated produce a fine sky-blue colour (*Thenard's blue, q.v.,* art. COBALT).

Aluminium compounds are usually colourless. Silicates and other compounds insoluble in acids require to be finely powdered, mixed with 4 parts of sodium carbonate or fusion mixture, and heated strongly in a platinum crucible. The aluminium, having thus become converted into sodium aluminate, is dissolved out with hydrochloric acid, evaporated to dryness to render any dissolved silica insoluble, and treated with dilute hydrochloric acid. The aluminium is then present as chloride.

Aluminous solutions, on addition of an alkali,

give a white gelatinous precipitate of hydrate, soluble in excess of the precipitant and in acids. Ammonia produces the same precipitate, which is only slightly soluble in excess, and is entirely reprecipitated on boiling off the excess of ammonia if sufficient ammonium chloride be present,

Estimation.—Aluminium is always precipitated as the hydrated oxide $Al_2O_3,3H_2O$.

For this purpose the solution, which, in presence of alkalis or alkaline earths, is mixed with excess of ammonium chloride, is treated with a *slight* excess of ammonia, and the solution boiled until the free ammonia is expelled. The hydrate, having thus become totally precipitated, is filtered, well washed, dried and heated in a platinum crucible, the heat being finally raised to bright redness for five minutes over the blowpipe. The weighed residue consists of anhydrous oxide, Al_2O_3, and contains 53 p.c. of aluminium. The separation from other metals is not difficult. The heavy metals may be precipitated from the *acid* solution by sulphuretted hydrogen, leaving the aluminium in solution, whilst the precipitation in presence of ammonium chloride in excess separates it from the alkalis and alkaline earths. From chromium and iron the separation is less simple. Chromium may be separated as follows :—The precipitated oxides are dried, mixed with 2 parts potassium nitrate and 4 sodium carbonate and fused in a platinum crucible. Alkaline chromate and aluminate are thus produced. The mass is digested with water and a small quantity of potassium chlorate and hydrochloric acid are then added, and the solution is evaporated to a syrup, with occasional addition of potassium chlorate to destroy the excess of hydrochloric acid and prevent its reducing action on the chromate. The aluminium in the diluted solution is precipitated as above by ammonia, leaving the chromate in solution.

For the separation from iron, the precipitated hydrated oxides are dissolved in the minimum quantity of hydrochloric acid and treated with an excess of *pure* strong potassium hydroxide solution, boiled for a few minutes, diluted, filtered, and well washed. The ferric oxide is thus precipitated and separated from the soluble alumina. The solution and washings are acidified with hydrochloric acid and precipitated by ammonia. On account of its solvent action upon glass, the treatment with potash should be performed in a porcelain dish, which is much less attacked, or, preferably, in one of silver.

Commercial Analysis of Aluminium.—The direct determination of aluminium, constituting as it does usually over 99 p.c. of the metal under examination, presents many difficulties. It has been proposed to estimate the aluminium by ascertaining the volume of hydrogen evolved on dissolving it in hydrochloric acid or the amount of chloride formed, but the errors to which such a determination is liable are too great to admit of sufficient accuracy ; moreover, the impurities usually present give rise to corrections which detract from the simplicity of the method and complicate the result. The solution in caustic soda is preferable to this, the iron and copper remaining as a black residue, but the silicon, in part, at least, reacts with caustic soda, so that even in this case the hydrogen evolved cannot

be taken as a measure of the aluminium present. In these circumstances it is customary to determine the impurities and arrive at the amount of aluminium by difference.

The impurities generally present in quantity are iron, silicon, and sometimes copper. Minute amounts of sodium, carbon, and nitrogen are also contained in the metal, but these should not greatly affect the result unless when dealing with specially impure metal. Commercially, therefore, iron and silicon alone are usually estimated. For the *iron*, the metal is dissolved in caustic soda, and this solution on acidulation with sulphuric acid yields sulphates of alumina and iron which redissolve in the acid, whilst the presence of copper is indicated by the appearance of a black residue. The amount of iron is finally determined by titration with potassium permanganate. For the *silicon*, the metal is digested with hydrochloric acid (in presence of nitric acid to avoid volatilisation of any silicon as chloride) forming a turbid solution owing to the separation of the silica. This is then boiled down with sulphuric acid until white fumes of this acid appear. The aluminium and iron salts are thus converted into sulphate, and redissolve on digestion with water, the silica being left in suspension.

After filtration and washing, the silica is strongly heated and weighed. *Copper* may be estimated as sulphide, or the black residue above mentioned may be dissolved and the copper estimated colorimetrically. If the amount of *sodium* is to be found, the metal must be dissolved in nitric acid to which a little hydrochloric acid is added. The solution is boiled down to dryness and exposed to a dull red heat so long as red fumes appear. The residue is extracted with water, care being taken finally to remove all alumina or other metals precipitated by the ordinary reagents. Ultimately the sodium salt remaining may be converted into sulphate and weighed as such. For fuller details a paper by Seligman and Willott may be consulted (Journ. Inst. Metals, vol. iii. p. 138).

For general analytical details, the following sources of information may be consulted : Moissan (Compt. rend. 121, 851); Gouthière (Analyst, 21, 270) ; Jean (Rev. Chim. Indust. 8, 5). The better qualities of commercial metal should not contain more than 0·5 p.c. of iron and silicon together, nor more than 0·03 p.c. of sodium.

Alloys.—The addition of quite small quantities of aluminium to certain metals (*e.g.* copper and iron) has a profound effect in modifying the properties of these metals. Likewise the addition of small quantities of certain metals (*e.g.* Fe, Mn, Si, &c.) to aluminium effects considerable change in the properties of this metal. The addition of 0·1 p.c. of aluminium to copper brings down its conductivity 23 p.c. ; the addition of zinc, copper, nickel, iron, or manganese to aluminium is accompanied by considerable augmentation of the tensile strength. The alloys of aluminium may be classified into bronzes, casting alloys, and rolling alloys, according to their properties. The *true bronzes* consist of copper and aluminium alone, but there are many binary (and ternary) alloys which contain metals other than copper and yet sufficiently resemble bronze to be classed along with

it. The bronzes proper chiefly employed are gold bronze, containing 3 to 5 p.c. of aluminium; steel bronze, with 8·5 p.c. Al and some silicon; acid bronze, with 10 p.c. Al. The copper bronzes, with 90, 92·5, 95 and 97·5 p.c. of copper, are all good alloys, showing homogeneity and freedom from crystallisation. They are of great hardness and high tensile strength.

Such alloys possess very valuable properties, the ultimate stress of the 90 p.c. alloy being 38 tons to the sq. inch, and they have the further valuable property of being practically noncorrodible by sea-water; this property is also shown very markedly by bronzes containing manganese. These bronzes in hardness and tensile strength compare favourably with the best steel, and are similarly affected by temper-ing. The alloys high in aluminium and low in copper are also of great commercial value; a bronze with 4 p.c. copper by rolling and drawing showed a steady increase in tensile strength from 9·6 tons to 20 tons to the sq. inch.

A small percentage of manganese renders these alloys more ductile without reducing their ultimate stress, but large proportions of man-ganese increase the strength and lessen the ductility.

For further information reference may be made to the eighth report of the Alloys Research Committee of the Inst. Mech. Engineers (Car-penter and Edwards), and to the ninth report (Rosenhain and Lantsberry), also to The Metal Industry, 1909, 186 (Hiorns). The composition of other bronzes used industrially is given in the following table :—

	Al	Cu	Zn	Sn	Ni	Cr	Mg
Hercules bronze .	2	65	33	—	—	—	—
Chromium bronze .	95·75	4	—	—	—	0·25	—
Duralum .	79	10*	—	—	—	—	11
Partinium .	88·7	6·8	4·5	—	—	—	—
Grossmann's alloy .	87	8	—	5	—	—	—
Argentan .	7	70	—	—	23	—	—
Hercules metal (No. 3)	1·5	61	37·5	—	—	—	—

* Phosphorised copper.

The aluminium alloy containing 20–50 p.c. of copper or nickel is brittle, as is the alloy with 35 p.c. of manganese.

Rolling Alloys.—Aluminium alloys, containing 3 to 4 p.c. of copper or 1·5 to 5 p.c. of nickel, roll well, as do many other alloys containing copper and zinc, the former in small quantity, amounting to from 1 to 3 p.c., and the latter 10 to 12 p.c., or even more.

Magnalium consists of aluminium alloyed with 2 to 10 p.c. of magnesium. This alloy is lighter than aluminium, and in strength and workability equal to good brass.

Casting alloys are also largely used, consisting most frequently of aluminium, zinc, and copper in varying proportions (Richards, Eng, and Mining Journ. 1908, 715). Magnalium admits of introduction with advantage of small quanti-ties of copper and nickel without unduly

raising its specific gravity. The tensile strength and hardness of these alloys are considerable, and they are said to be resistant to atmospheric corrosion (Barnett, J. Soc. Chem. Ind. 1905, 832). Taps, tuyères, and the like are made from an alloy composed of aluminium, to which 12 p.c. Cd., 6 p.c. Cu, 5 p.c. Sn, 2 p.c. Ni are .dded. Pedestals are also made of aluminium, ;ontaining 14 p.c. Sb, 1·2 p.c. Cu, 12 p.c. Sn, 37 p.c. Zn, and 0·8 p.c. Pb; copper, with 10 p.c. Al and 1 p.c. Mn, is an excellent hard alloy for bearing metal or tool steel; horse-shoes are made from a ternary alloy of aluminium con-:aining either 12 p.c. Cu and 10 p.c. Zn, or 5 p.c. Cu and 10 p.c. Sn. Aluminium or its alloys ave proved useful where there is contact with concentrated nitric acid, or for stills and plant used in the sulphite pulp manufacture; also where stearic or other organic acids are dealt with. These alloys resist acid corrosion to a remarkable degree, and even if cooking utensils were made from an aluminium copper alloy, Carpenter and Edwards have shown that if corrosion does occur the copper is not dissolved out, and hence there is no danger of poisoning in using such vessels, since the salts of aluminium have no toxic action.

An improvement is effected by the addition of aluminium to *brass.* An alloy containing aluminium 2·5 p.c., copper 70 p.c., and zinc 27·5 p.c., is said to show nearly double the tenacity and considerably more than double the elongation of ordinary cast brass.

The presence of *tin* in aluminium renders it more fusible and brittle. According to Bourbouze (Compt. rend. 102, 1317), an alloy of aluminium 100 and tin 10 is strong, easily worked, may be soldered as easily as brass, is whiter and less affected by reagents than aluminium, and is very suitable for parts of optical instruments. Its sp.gr. is 2·85. The addition of aluminium to tin increases its hardness and tenacity. The alloys containing 5, 7, and 9 p.c. of aluminium are all easily worked and soldered. A larger proportion of aluminium is liable to separate out on melting.

Aluminium combines in all proportions with *cadmium*, forming malleable fusible alloys.

Small quantities of *silver* increase the hardness and elasticity and lower the melting-point without rendering aluminium brittle. The alloy containing 4 p.c. silver has been used for the beams of delicate chemical balances. When the addition exceeds 5 or 6 p.c. the metal becomes brittle; the 50 p.c. alloy is as hard as bronze, but very brittle. ' *Tiers argent*' consists of 1 part silver and 2 parts aluminium; it is of considerable hardness, and is used for table-spoons, &c. The addition of 5 p.c. of aluminium to silver renders it as hard as standard silver and very permanent.

The presence of aluminium in *gold* consider-ably alters its properties. The addition of 0·186 p.c. of aluminium to *pure* gold increases the tensile strength from 7 tons to 8·87 tons per square inch, a greater increase than is produced by the same amount of any other metal (Roberts-Austen, Roy. Soc. Rep. April, 1888; Chem. News. 1888, v. 57, p. 133). With 1 p.c. alu-minium the gold has the colour of ' green gold,' is hard but easy to work; with 5 p.c. aluminium it is white and extremely brittle, and with 10 p.c.

white, brittle, and crystalline. Aluminium containing 10 p.c. of gold is white and hard.

The malleability of aluminium is not much impaired by the addition of gold, silver, or tin, but the presence of iron, and especially of silicon, is very injurious.

With *silicon* aluminium unites in almost all proportions, either directly or by its action on silicious materials; for this reason the fusion or preparation of this metal should not be performed in any silicious crucible in presence of a flux. The presence of silicon renders aluminium brittle and much less permanent. The alloy containing 10 p.c. silicon is grey and brittle. Wöhler prepared an alloy containing 70 p.c. silicon, which still appeared metallic.

With *iron* the alloys are of especial interest. The presence of a small quantity of iron is very injurious; it renders the aluminium crystalline, and raises the melting-point. The alloy containing 5 p.c. of iron is hard and brittle; with 8 p.c. the alloy crystallises in needles, and on heating separates into a more liquid alloy containing but little iron and a skeleton very rich in that metal. Michel (Annalen, 115, 102) has prepared an alloy which crystallises in six-sided prisms, corresponding to Al_2Fe. A beautifully crystalline substance having the composition Al_4Fe is often found in the neighbourhood of the cathode of a reduction furnace.

The valuable properties imparted to iron and steel by the presence of a small quantity of aluminium have long been known; Faraday (Quarterly Journ. Roy. Inst. 1819, 290) found from 0·013 to 0·069 p.c. of aluminium in certain samples of Bombay wootz, though it has been shown by Henry and others that this metal is not always present. About the same time S. B. Rogers showed the presence of aluminium in some of the best quality of pig-iron made in South Wales, and found that a steel to which 0·8 p.c. of aluminium had been added in the form of an alloy with iron, was rendered harder and stronger and resembled the best wootz (Rogers, Metallurgy, 1858, 14). A superior steel was prepared by Sir Charles Knowles, which was stated to owe its value to the use of *kaolin* and consequent introduction of aluminium into the metal in its preparation (Mining Journal, 1859, 118).

Messrs. Cowles Bros. have exhibited a Siemens-Martin basic steel containing 0·2 p.c. aluminium, which welds with iron and shows no mark at the junction.

The addition of aluminium to iron or steel for the production of ' mitis castings ' has been patented by P. Ostberg (Engineering, 1886, 360). Iron and steel, especially at temperatures far above the melting-point, absorb considerable quantities of gas, which impairs the value of the castings. The addition of 0·05 or 0·1 p.c. of aluminium to the fused iron or steel lowers the melting-point, prevents the absorption of gas, and considerably increases the fluidity. The metal can then be easily cast.

Nickel and aluminium combine with incandescence when heated together. The presence of under 3 p.c. of nickel lowers the melting-point and increases the hardness and elasticity.

Pure aluminium combines with mercury, although not readily, when the metals are heated together in an inert gas such as carbonic anhydride. The two metals combine rapidly in presence of alkalis. The amalgam may also be produced by electrolysis of mercuric nitrate, using a negative plate of aluminium dipping in mercury. When aluminium is rubbed with wash leather impregnated with mercury, combination occurs; the surface rapidly oxidises and becomes heated, with formation of concretions of alumina (John and Hinze, Ber. 7, 1498).

Alloys of *bismuth* with aluminium are hard and brittle. With *antimony* and *lead* aluminium does not unite, although traces of lead are frequently present in commercial aluminium.

Sodium unites readily with aluminium. The last traces of sodium are difficult to remove, especially, it is said, when the metal has been reduced from cryolite. The alloys are easily attacked by moisture, and burn in the air, with oxidation both of the aluminium and sodium; that containing 2 p.c. of sodium decomposes water with ease. The necessity of avoiding the presence of sodium in the preparation of aluminium is therefore obvious.

Aluminium also unites with *manganese*; with *platinum* it unites easily, forming fusible alloys. With *boron* aluminium combines in varying proportions. The so-called ' adamantine ' and ' graphitic ' boron appear to be borides of aluminium (Hampe, Annalen, 1876, 75; and Deville and Wöhler, *ibid.* 1867, 268) (*v.* BORON).

Mallet (Chem. Soc. Trans. 1876, ii. 350) has prepared a nitride of aluminium in small crystals hard enough to scratch glass.

For further information, see J. W. Richards, Aluminium and its Alloys, London.

Aluminium oxide, *Alumina*, Al_2O_3.

Aluminium forms only one oxide, Al_2O_3, corresponding to and isomorphous with the sesquioxides of iron and chromium.

This oxide occurs native, colourless as *hyaline*, *corundum*; or coloured by metallic oxides, as *ruby*, *sapphire*, *oriental topaz*, &c. (*q.v.*). Very impure, dark, and usually associated with magnetite and *hæmatite*, it occurs in large boulders in many districts, and is used as a grinding and polishing material in the form of *emery* (*q.v.*). The native oxide crystallises in the rhombohedral system; in hardness it comes next to the diamond. The finely coloured specimens are used as gems. It occurs almost pure in considerable quantities in the Alleghanies in Northern Georgia.

It may be prepared by the ignition of aluminium foil in air or oxygen; the oxide so produced is fused and as hard as corundum.

Amorphous alumina may be produced by ignition of the precipitated hydrate, pure aluminium sulphate or ammonia alum; in either case alumina alone is left.

It is white and soft, but becomes hard on strong ignition. According to H. Rose (Pogg. Ann. 74, 430) the sp.gr. of the oxide after heating over a spirit-lamp is 3·725; its density may be raised to 4, just about that of corundum by heating in a porcelain furnace, but it still remains amorphous. It is remarkable that though the density of the artificially prepared alumina is nearly 4, its bulk density may be less than one-fifth of this. With a somewhat lower density the bulk density is higher, but is still such that it occupies a larger bulk than the same weight of water.

When heated by the oxyhydrogen blow-pipe, alumina melts and crystallises; the addition of chromium oxide or a chromate imparts a ruby colour to the crystals.

Fremy and Verneuil (Compt. rend. 1888, 566) have prepared artificial rubies by heating to redness a mixture of barium fluoride and alumina containing a trace of potassium dichromate. The heat requires careful management. Fine rubies are thus formed in a friable matrix which may be separated by agitation with water. By former methods the matrix was hard and difficult to remove (Fremy and Feil, Compt. rend. 1877, 1029, and 1887, 737). The crystals contain no barium, easily scratch the topaz, and possess the form and properties of natural rubies; their crystalline form has been determined by Descloiseaux (Compt. rend. 1888, 567). By the addition of a little cobalt oxide before the fusion, sapphires may be produced.

Alumina is soluble, when strongly heated, in boric acid; the latter may be driven off at a very high temperature, leaving crystalline alumina. By the addition of the proper oxide the corresponding spinels may be produced, coloured by cobalt oxide (blue), chromium oxide (red), iron oxide (black), (Ebelmen, Ann. Chim. Phys. 3, 22, 211 and 33, 34). Only two *hydroxides* of aluminium are known, viz.: Al_2O_3,H_2O and $Al_2O_3,3H_2O$. By Graham's method an aqueous solution of the hydroxide may be obtained.

When the hydroxide is freshly precipitated it dissolves readily in dilute acids, but on standing, or after filtration, solution is more difficult, and is best achieved by a mixture of 8 parts of sulphuric acid and 3 parts of water. When heated, the hydroxide loses its water, undergoing a contraction of about 30 p.c. in bulk as it passes into the form of the anhydrous oxide.

When boiled with water containing a drop of a 1 p.c. solution of alizarin, the hydroxide assumes a bright red colour, not removed by a weak solution of acetic acid.

This test easily distinguishes it from gelatinous silica. Aluminium hydroxide possesses a powerful affinity for many organic substances, and enters into association with a large number of colouring matters, precipitating them entirely as *lakes*. On this property depends the use of alum mordants (red liquor, &c.). They precipitate the hydroxide upon the fibre of the goods to be dyed, and this constitutes the *mordant* or fixing agent which retains the colour.

Sodium aluminate $Al_2O_3,3Na_2O$ or $Al_2(NaO)_6$. This salt is now prepared on a large scale, both to be used as such and as an intermediate product in the preparation of the sulphate and other salts of aluminium.

Its formation depends upon the property possessed by alumina of acting as an acid in presence of a powerful base.

Its preparation from bauxite has been described on page 106. It may also be produced by passing a current of steam through a heated mixture of bauxite and common salt, and by strongly heating a mixture of bauxite, sodium sulphate, and carbon, but in the latter case its purification from the sodium sulphide simultaneously produced is difficult. It is also formed in the preparation of soda from *cryolite*. According to Thomsen's method, powdered cryolite is

heated to redness with chalk, forming sodium aluminate and calcium fluoride:—

$$Al_2F_6 \cdot 6NaF + 6CaCO_3 = Al_2(NaO)_6 + 6CaF_2 + 6CO_2$$
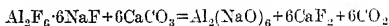
The mass produced is lixiviated with water and filtered. From this aluminate the hydroxide is precipitated by carbon dioxide with formation of sodium carbonate:—

$$Al_2(NaO)_6 + 3CO_2 + 3H_2O = Al_2(OH)_6 + 3Na_2CO_3$$
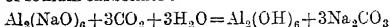
The hydroxide is usually made into aluminium sulphate by solution in sulphuric acid, or it is converted into alum.

An entirely different process has been introduced by Sauerwein. The finely powdered cryolite is boiled with milk of lime forming aluminate as before:—

$$Al_2F_6 \cdot 6NaF + 6CaO = Al_2(NaO)_6 + 6CaF_2.$$
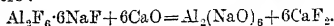
For the conversion of the aluminate into oxide Sauerwein applies a peculiar property possessed by that salt, which shows the readiness with which alumina loses its acid properties and again becomes basic. Sodium aluminate, when mixed in equivalent proportions with any haloid salt of aluminium, is decomposed; the sodium combines with the halogen, while the whole of the aluminium is precipitated as hydroxide. On the large scale the haloid salt used is cryolite. The finely powdered mineral is stirred into the clear liquid from the previous operation, and the alumina precipitated as hydroxide:—

$$Al_2(NaO)_6 + Al_2F_6 \cdot 6NaF + 6H_2O$$
$$= 2Al_2(OH)_6 + 12NaF.$$
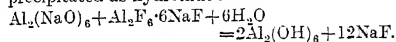
Sodium aluminate is a white, infusible, amorphous solid, easily soluble in both cold and hot water. The concentrated solution rapidly deposits alumina, leaving in solution a basic aluminate, which on evaporation is obtained as a fusible and hygroscopic mass. The addition of any acid at once decomposes it with precipitation of alumina. This alumina is pure and free from alkali, which is never the case when alkaline precipitants have been used. It may be employed as a mordant in dyeing and calico-printing, in an acid and not, as in the case of alum, an alkaline bath. For the production of *lakes* the colouring matter is mixed with the aluminate solution and precipitated by the addition of sulphuric acid. According to Morin these lakes are richer than those obtained from alum and are produced at about one half the cost.

Potassium aluminate $Al_2O_3 \cdot 3K_2O$ or $Al_2(KO)_6$ is obtained in hard glistening crystals when alumina is fused with potash, the mass boiled in water and the solution evaporated *in vacuo*.

Aluminium chloride Al_2Cl_6. This compound was first prepared in 1824 by Oersted, by passing chlorine over a mixture of alumina and charcoal heated to redness. The method and apparatus resemble that used in the preparation of the double chloride, omitting the sodium chloride.

According to P. Curie (Chem. News, 28, 307) it may be easily prepared as follows:—Anhydrous alumina, or, less satisfactorily, clay, is strongly heated in a tube and subjected to a current of hydrochloric acid impregnated with carbon disulphide by bubbling through that liquid. Aluminium sulphide appears to be formed and at once decomposed by the hydrochloric acid, yielding aluminium chloride and sulphuretted hydrogen. The condensed chloride

may be freed from sulphur by distillation with iron filings.

A solution of the chloride may be obtained by dissolving the hydroxide in hydrochloric acid.

The pure anhydrous chloride is a white, waxy, crystalline solid ; in presence of a trace of iron it becomes yellowish. On heating, it volatilises without fusion. If large pieces be quickly heated they fuse and boil at 180° to 185° (Liebig). It is very hygroscopic, and evolves hydrochloric acid on exposure to the air ; is easily soluble in water ; soluble in alcohol and ether. When deposited from a solution in hydrochloric acid, it forms crystals of the formula $Al_2Cl_6,12H_2O$.

It absorbs ammonia and combines with many metallic chlorides, forming double chlorides, the most important being that with sodium. Aluminium chloride has been recommended by Filsinger (Chem. Zentr. 10, 1270) for the preservation of wood, and by Saget (Chem. News. 45, 113) and others (J. Soc. Chem. Ind. 1882, 185 and 230) for the production of a discharge on indigo blue. An impure chloride containing calcium and sodium salts is stated to be largely used as a disinfectant under the name ' Chloralum.'

Double chloride of aluminium and sodium $Al_2Cl_6,2NaCl$. This compound may be produced by fusing together the proper proportions of aluminium and sodium chlorides. It is a colourless crystalline solid, melting at 185° (Deville) and volatilising at a red heat. It is slightly hygroscopic, but much less so than aluminium chloride ; it is also more stable and more satisfactory in use than that substance, and gives up nearly the whole of its aluminium when reduced by sodium.

Aluminium bromide Al_2Br_6 is most readily prepared by the action of bromine on metallic aluminium. The action is violent, and the metal should only be added gradually. A lump of aluminium weighing twenty grams becomes strongly heated and even fused on being placed in cold bromine (Mallet, Phil. Trans. 171, 1018).

It may also be prepared by the action of bromine on a strongly heated mixture of alumina and carbon, and, in solution, by dissolving the hydroxide in hydrobromic acid. It crystallises in colourless shining laminæ, which melt at 93° (Deville and Troost) and boil at 263·3° (at 747 mm.) (Mallet).

Like the chloride, it forms a double bromide, $Al_2Br_6,2KBr$.

Aluminium iodide Al_2I_6 may be prepared by heating aluminium with iodine in a closed tube. It melts at about 185° (Weber) and boils at 350° (Deville and Troost) ; its vapour is combustible. It dissolves in water, alcohol, and carbon disulphide.

Aluminium fluoride Al_2F_6, may be prepared by the action of gaseous silicon fluoride, or of hydrofluoric acid upon aluminium. It forms transparent rhombohedra, volatile at a red heat, insoluble in water and unacted upon by acids. In solution in hydrofluoric acid, it appears to form the compound $Al_2F_6·6HF$, the acid corresponding to the double fluoride of aluminium and sodium.

Cryolite $Al_2F_6·6NaF$. This important compound may be prepared artificially, and attempts have been made to produce it as a substitute for the natural cryolite, it being claimed that the artificial cryolite possesses the advantage

of being lighter and melting at a lower temperature (J. Soc. Chem. Ind. 1890, 945). Natural cryolite occurs in quantity only in one locality, in a large vein in the gneiss at Ivigtut in Greenland. Greenland cryolite has the following composition : Al 13·2, Na 32·7, F 54·2, and small quantities of manganese. The melting-point of mixtures of cryolite and alumina is said to be—

Cryolite				1000°
With 3 p.c. Al_2O_3	.	.	974°
,, 6 p.c. ,,	.	.	960°
,, 10 p.c. ,,	.	.	980°
,, 15 p.c. ,,	.	.	994°
,, 20 p.c. ,,	.	.	1015°

(Chem. Soc. Abst. 1907, 469).

It is a semi-transparent, white, crystalline, brittle solid, which melts at the edges in a candle flame. Its hardness is 2·5 to 3 ; its sp.gr. 2·95. When impure it is frequently yellowish-red or even black (v. CRYOLITE).

Cryolite is used as a flux in the manufacture of aluminium ; formerly for making salts of sodium and aluminium ; and for the manufacture of an opaque, porcelain-like glass. It is also used for enamelling pans and as a glaze for pots as replacing lead glaze. (See further, Benzon, (Hoffmann's Ber. Enew. Chem. Ind. [1] 660).)

Aluminium sulphide Al_2S_3, may be prepared by strongly heating a mixture of aluminium and sulphur, or by heating alumina to bright redness in the vapour of carbon disulphide. It forms a yellow, glassy mass, which fuses with difficulty, and burns in air with production of alumina and sulphur dioxide. It is at once decomposed by water. Houdard (Compt. rend. 1907, 801) found that by heating aluminium turnings and sulphides of manganese iron and chromium in a carbon boat, sulphides related to the spinels are formed, of which he prepared

$$MnS,Al_2S_3, \quad FeS,Al_2S_3, \quad CrS,Al_2S_3.$$
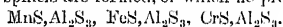
Aluminium carbide Al_4C_3 may be obtained by the action of carbon or the oxides of carbon on alumina at very high temperatures, and often occurs in small quantity in the neighbourhood of the cathode of aluminium reduction furnaces in the form of a yellow powder ; it is formed when a mixture of alumina and carbon is submitted to a current of 300 amperes at 35 volts. It possesses the remarkable property of being stable at high temperatures, and yet undergoing decomposition at a dull red heat. It reacts, though somewhat slowly, with water or dilute acids with the production of methane. The formation of carbide and ultimately its decomposition has been proposed as a means of preparing alumina from clay or other crude materials. Pring (Chem. Soc. Trans. 1905, 1530) found that up to 1400°C. the carbide acts as a reducing agent on metallic oxides,

$$Al_4C_3 + 12MO = 2Al_2O_3 + 3CO_2 + 12M,$$
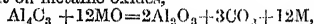
but at higher temperatures alloys of aluminium and the metal are produced, only carbon being oxidised,

$$Al_4C_3 + 3CuO = Al_4Cu_3 + 3CO,$$
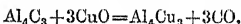
owing to the fact that alumina can be reduced by carbon at very high temperatures ; at lower temperatures the aluminium is oxidised by carbonic oxide as observed by Moissan,

$$6Al + 3CO = Al_4C_3 + Al_2O_3,$$
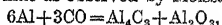
the reaction being reversed at the higher temperatures.

Aluminium sulphate $Al_2O_3(SO_3)_3,18H_2O$ or $Al_2(SO_4)_3,18H_2O$. Aluminium sulphate occurs naturally in considerable quantities. As the hydrated salt of the above composition, it forms the chief constituent of the mineral *alunogen, halotrichite, feather alum,* or *hair salt,* which is found in volcanic districts, at Bilin in Bohemia, Copiapo in Chili, &c. It also occurs in pyritic shale. A sample of feather alum from Friesdorf, Bonn, was found by Rose to contain Al_2O_3 14·9 p.c., SO_3 37·4 p.c., FeO 2·5 p.c., H_2O 45·2 p.c., with traces of K, Na, Mg, and SiO_2.

Aluminite or websterite, a hydrated basic salt of the composition $Al_2O_3SO_3,9H_2O$, has been found at Auteuil, Halle, Muhlhausen, &c.

In combination with potassium sulphate, the basic salt occurs also in *alunite, alumstone,* or *alum rock* $K_2SO_4,3Al_2O_3(SO_3),6H_2O$, a mineral which is found in large quantities at La Tolfa near Civita Vecchia, in Hungary, at Puy-de-Sancy and Madriat in Auvergne, and in many other localities. It usually occurs in fibrous compact masses in trachyte, of colour varying from white to red or brown, being produced by the action of sulphurous gases upon trachytic rocks rich in felspar.

The alunite from La Tolfa contains from 35 p.c. to 17·5 p.c. alumina; the average composition of the mineral is Al_2O_3 27·6 p.c., SO_3 29·74 p.c., K_2O 7·55 p.c., Fe_2O_3 1·2 p.c., SiO_2 22·7 p.c., H_2O 11·2 p.c.

Aluminium sulphate may be produced by dissolving either the hydrated oxide or the silicate in sulphuric acid. Of the raw materials available for its manufacture, the two which are of the greatest importance at the present time are china clay (kaolin) and bauxite. China clay is a very pure variety of clay, resulting from the natural decomposition of felspar, and approximating in composition to the formula $Al_2O_3,2SiO_2,2H_2O$. It is of comparatively rare occurrence, being found chiefly in Devon and Cornwall in England; at St. Yrieix near Limoges, and in the departments of Allier, Puy-de-Dome, and Brittany, in France; at Seilitz in Saxony; and at Nassau in Bavaria.

Bauxite is an impure aluminium hydroxide $Al_2O_3,2H_2O$, containing widely varying quantities of silica and ferric oxide. It is found in Ireland, in the south of France, and in Austria, Calabria, Senegal, &c. (*v.* BAUXITE).

The composition of typical commercial grades of the two minerals is given in the following table, the analyses having been made on material dried at 100°:—

	China clay		Bauxite	
Source				
	St.Stephen's	St.Austell	Antrim	France
Al_2O_3	40·15	41·10	41·08	64·18
Fe_2O_3	0·35	0·20	3·21	3·47
SiO_2	45·00	46·20	}33·17	18·96
TiO_2	—	—		
K_2O+Na_2O	0·80	trace	—	—
H_2O (comb.)	13·70	12·50	22·54	13·39
Total	100·00	100·00	100·00	100·00

Production of aluminium sulphate from china clay.—At the present time the manufacture of aluminium sulphate from china clay is carried out on an extensive scale by a process based upon the original patent of Pochin (Pat. 1855, 14656). The clay, containing about 40 p.c. alumina, is obtained from Cornwall, and is selected as free as possible from grit and oxide of iron. It is reduced by milling and sifting to the finest possible state of division, and after a preliminary drying by exposure to a warm atmosphere, is calcined at a dull-red heat in a reverberatory furnace. The furnace is provided with three working doors, the material being introduced by the door which is most remote from the firegrate, and gradually raked forward until it reaches the hottest part of the hearth. During the calcination the clay suffers a loss in weight amounting to from 20 to 25 p.c., due to the expulsion of the whole of the moisture present (10 to 15 p.c.) and of the greater part of the water of hydration.

The calcined clay, which still contains about 3 p.c. of water, is transferred by means of iron tubs to a lead-lined wooden vat containing the requisite quantity of sulphuric acid, heated to a temperature of 85°, and having a strength at this temperature of 96°Tw. A vigorous reaction immediately takes place, and after the lapse of 15 minutes, during which period the contents of the vat are kept well agitated, the product is run into lead-lined wooden waggons (with removable sides), in which the reaction continues for a considerable time and the pasty mass gradually solidifies. Finally the solid block is brought under a heavy mechanical knife, and by a combined cutting and crushing action is reduced to the state of a coarse powder.

The product, which is brought on the market under the name of 'alum cake,' contains the whole of the silica, iron, and other impurities present in the clay, its average composition being: Al_2O_3 (soluble) 12·25 to 13·0 p.c., Fe_2O_3 0·12 to 0·22 p.c.; combined SO_3 29·5 to 31·8 p.c., free SO_3 0·4 to 1·0 p.c.; insoluble matter 20·0 to 26·5 p.c.

About 60 p.c. of the alumina present in the china clay is converted into sulphate.

The commercial 'white sulphate of alumina' is prepared from alum cake in the following manner: The coarsely crushed alum cake is lixiviated with water (or with weak liquors from previous extractions) in lead-lined vats heated by live steam; after settling, the clear solution is decanted by means of a hinged pipe, and run into lead-lined evaporators, heated by steam coils, where it is concentrated to a strength of 112°Tw. at the boiling-point (about 115°). The syrupy liquid is then run into a series of shallow tiled troughs, where it solidifies on cooling. Before solidification occurs, a number of leaden partitions are inserted in the troughs, and the product is thus obtained in the form of rectangular blocks of uniform size (24″ × 9″ × 6″). 'White sulphate of alumina,' prepared by the above process, contains on an average about 14 p.c. of alumina and 0·25 p.c. of ferric oxide, and is practically free from insoluble matter. Another grade of the material is prepared containing 17·5 p.c. alumina.

Preparation of aluminium sulphate from bauxite.—The substitution of bauxite for china

I 2

clay in the manufacture of aluminium sulphate was proposed by Lechatelier in 1858, and its treatment forms the subject-matter of numerous patents. Bauxite has the advantage over china clay that it is more readily soluble in acid, and needs no preliminary calcination, the chief drawback to its use being the presence of a comparatively large amount of iron.

The treatment of bauxite for the preparation of ' alumino-ferric cake,' as patented by Messrs. P. and F. M. Spence (1875), is as follows :—The mineral is digested with dilute sulphuric acid with the aid of steam until the acid is neutralised ; the insoluble matter allowed to subside, and the solution evaporated to 100°Tw. and run into shallow-partitioned lead coolers. It there solidifies, and is removed in blocks 18 or 20 inches square, each weighing about 1 cwt. It is yellowish-green in colour, contains much alumina, and a small proportion of iron and free acid. It is used in the preparation of all but the finest papers, in the precipitation of sewage and refuse liquids, and in the clarification and decolourisation of water supplies. The following analysis shows its general composition : Al_2O_3 14·26 p.c. (corresponding to $Al_2O_3 3SO_3$ 47·61 p.c.), Fe_2O_3 0·28 p.c., FeO 0·32 p.c. SO_3 (combined) 35·36 p.c., SO_3 (free) 0·45 p.c. Insoluble 0·06 p.c.

The commercial sulphate of alumina which is sold under the names of ' concentrated alum ' and ' alferite,' resembles alumino-ferric in composition, and is prepared by a similar process. The following details concerning its manufacture will serve to exemplify modern practice.

As raw material, it is usual to employ a mixture of Irish and French bauxites, reduced by means of disintegrators to the state of a coarse powder. The powdered mineral is conveyed by means of an elevator to a lead-lined vat containing sulphuric acid, heated to its boiling-point (about 112°), and having a strength, at this temperature, of 96°Tw. The mixture of acid and bauxite is boiled vigorously for 6 hours, after which it is diluted with weak liquors to 70°Tw. (measured at the boiling-point) and allowed to settle. The clear liquor is decanted and evaporated in lead-lined vessels until its density reaches 112°Tw. (boiling). It is then run into partitioned coolers where it solidifies, forming blocks or slabs, containing on an average 13·8 p.c. alumina, 0·7 p.c. ferric oxide, and 0·1 p.c. insoluble matter.

If French bauxite be used alone in the above process, great difficulty is experienced in the clarification of the liquor ; with a mixture of Irish and French bauxites, however, rapid settling occurs, and a perfectly clear liquor is readily obtained. It is of importance also, in this connection, that the liquor should retain a small amount of free acid, as the fully neutralised solution settles very slowly.

Sulphate of alumina prepared by any of the above processes always contains appreciable quantities of iron, and the removal of this impurity is a problem of considerable importance, and one which has received the attention of many chemists. Numerous processes have been devised for the purpose, but it is doubtful if any of these is satisfactory in works' practice.

Newlands (Eng. Pat. 1880, 5287) evaporates a crude solution of the sulphate to a density of 67°Tw. (at 200°F.) and cools for twenty-four hours in leaden tanks.

About 60 p.c. of the sulphate thus crystallises out. The liquid is drained off, and the residue pumped or forced into lead-lined filter presses, the plates of which are covered with thick felt, and separated by metal rings. Here it is subjected to a pressure of about 200 lbs. to the square inch. The hard cake so produced contains about 67 p.c. of the total aluminium sulphate, and 0·05 to 0·1 p.c. of iron. The mother liquor, evaporated and similarly treated, yields a second and third crop of crystals containing increasing quantities of iron.

Chadwick and Kynaston have patented a method for the removal of iron from bauxite before converting the latter into aluminium sulphate. The powdered mineral is mixed to a thick cream with water, and treated with 5 to 10 p.c. of oxalic acid and sufficient hydrochloric acid to prevent the formation of insoluble oxalates. After seven to ten days the mass is washed, and a large proportion of the iron (together with some of the alumina) is thus removed as oxalate.

Condy, in 1877, proposed the reduction of the iron by reducing agents, or its conversion into sulphide by sulphuretted hydrogen, and the removal of the metal or sulphide by dilute acid. The proportion of iron may thus be reduced to one-third.

Weismann suggested the precipitation of the iron from aluminium sulphate liquors by means of potassium ferrocyanide. The method is by no means satisfactory, as the precipitate contains much alumina and subsides very slowly.

Kynaston precipitates the bulk of the iron as ferric arsenite, removing the last portions with calcium ferrocyanide, followed by the addition of copper or zinc sulphate.

According to Fahlberg and Semper (Eng. Pat. 1881, 5579). both ferrous and ferric salts may be precipitated from aluminium sulphate by agitation in the cold for about thirty minutes with lead peroxide, ferrous salts being first oxidised and then precipitated. No lead passes into solution unless chlorides be present. The composition of the precipitate is not known, but the peroxide may be regenerated by digestion in cold nitric acid. P. and F. M. Spence (Eng. Pat. 1882, 3835) use manganese dioxide for the same purpose. In presence of reducing agents such as ferrous salts, &c., manganese passes into solution, and requires to be reprecipitated by addition of chlorine or a hypochlorite.

The use of metantimonic acid and metastannic acid (Hood and Salamon) has also been proposed for the precipitation of iron. The iron is first oxidised by the addition of bleaching powder, and the liquid is neutralised with chalk and agitated with the precipitant. Both substances may be regenerated by digesting the precipitate with sulphuric acid.

(For further information regarding these processes, *see* Beveridge (J. Soc. Chem. Ind. 1886, 16–22) ; B. E. R. Newlands (*ibid.* 1882, 124) ; Kynaston (Chem. News, 40, 191 and 202).)

The above-mentioned processes for the

purification of aluminium sulphate from iron possess little or no commercial significance at the present time. 'Pure aluminium sulphate' is prepared directly from *pure* alumina, which is obtained from bauxite by the 'alkali fusion' process. The bauxite, reduced to a fine powder, is mixed with soda ash in such proportions that for every molecule of Al_2O_3 (including Fe_2O_3) present there are 1 to 1·2 molecules of Na_2O. The mixture is strongly heated in a reverberatory furnace, with frequent stirring, for a period of five hours. Carbon dioxide is evolved and the alumina and ferric oxide are converted into sodium aluminate and sodium ferrite respectively. The mass is lixiviated by successive extractions, first with weak liquor from previous batches, and finally with pure water. The sodium aluminate dissolves as such, whilst the sodium ferrite is decomposed, forming insoluble ferric oxide which remains in the exhausted residue, and caustic soda which passes into solution. The clear liquor is run into a boiler and saturated with carbon dioxide produced by the combustion of coke or by the decomposition of limestone. During the passage of the gas the contents of the boiler are heated to 70° and kept thoroughly stirred by means of an agitator. When the precipitation of the alumina is complete, the liquid is allowed to settle and the clear liquor decanted and concentrated for the recovery of the dissolved sodium carbonate, whilst the alumina is drained in a hydro-extractor.

A cheaper process for obtaining the alumina from the sodium aluminate has been devised by Bayer (as described, p. 106).

The alumina prepared by either of the above processes yields by treatment with sulphuric acid, a very pure quality of aluminium sulphate. Two grades of the latter are commonly prepared for the English market—the one, sold in the form of slabs or blocks, contains 14·0 p.c. of alumina and 0·0025 p.c. of ferric oxide, the other, sold in powder, contains 18·0 p.c. of alumina and 0·0040 p.c. of ferric oxide.

Aluminium sulphate crystallises with difficulty in thin, six-sided nacreous plates, containing 18 molecules of water and having a density of 1·6913 at 17° (Dewar). The following table of solubilities is given by Poggiale (Ann. Chim. Phys. [3] 8, 467) for the crystalline and anhydrous salts:—

Temp. °C.	Solubility in 100 parts of water	
	$Al_2(SO_4)_3$	$Al_2(SO_4)_3,18H_2O$
0	31·3	86·8
10	33·5	95·8
20	36·1	107·3
30	40·4	127·6
40	45·7	167·6
50	52·1	201·4
60	59·1	262·6
70	66·2	348·2
80	73·1	467·3
90	80·8	678·8
100	89·1	1132·0

The addition of alcohol, in which aluminium sulphate is almost insoluble, to aqueous solutions of aluminium sulphate, facilitates the crystallisation of the salt (Persoz).

Karl Reuss (Ber. 17, 2888) gives the density of solutions of pure anhydrous aluminium sulphate as follows:—

Per-centage	Density at 15°C.	Per-centage	Density at 15°C.
1	1·017	14	1·1467
2	1·027	15	1·1574
3	1·037	16	1·1668
4	1·047	17	1·1770
5	1·0569	18	1·1876
6	1·0670	19	1·1971
7	1·0768	20	1·2074
8	1·0870	21	1·2168
9	1·0968	22	1·2274
10	1·1071	23	1·2375
11	1.1171	24	1·2473
12	1·1270	25	1·2572
13	1·1369		

Per-centage	Density at 25°C.	Density at 35°C.	Density at 45°C.
5	1·0503	1·0450	1·0356
10	1·1022	1·0960	1·0850
15	1·1522	1·1460	1·1346
20	1·2004	1·1920	1·1801
25	1·2483	1·2407	1·2295

When heated, aluminium sulphate melts in its water of crystallisation, swells up, and gradually forms a white porous mass of the anhydrous sulphate, which only dissolves slowly in water. At a red heat oxides of sulphur are expelled and a residue of pure alumina remains.

Aluminium sulphate combines readily with the sulphates of the alkali metals, forming crystalline double sulphates, known as alums, which are, as a rule, considerably less soluble than aluminium sulphate itself. According to Reuss (Ber. 17, 2888), the addition of 1 p.c. of potassium sulphate to a solution containing 7 p.c. or upwards of aluminium sulphate, at once produces a crystalline precipitate of alum.

The general industrial uses of aluminium sulphate are the same as those of ordinary alum. It is largely used in paper-making and in the preparation of red liquor as a mordant. The coarser preparations are employed for the precipitation of sewage.

For the detection of free acid in aluminium sulphate, Miller (Ber. 1883, 1992) recommends the use of methyl orange, which yields an orange-coloured solution with the pure sulphate, but is reddened by free acid. A dilute solution of Congo red becomes blue in presence of free acid, but is not affected by the pure salt.

For the estimation of the free acid, a weighed quantity (20 to 50 grams) of the sample is dissolved in 40 to 100 c.c. of water, the solution heated to boiling, and titrated with normal caustic soda until a drop of the liquid, taken out with a glass rod, fails to yield a blue colour when mixed with six drops of Congo red solution (prepared by dissolving 0·067 gram. of Congo

red in 100 c.c. of boiling water and diluting to a litre).

T. J. I. Craig (J. Soc. Chem. Ind. 1911, 184) proposes to determine the free acid in aluminium sulphate by treating the latter with excess of neutral potassium fluoride, whereby the double salt AlF_3·$3KF$ is formed together with potassium sulphate. As these products are neutral to phenolphthaleïn, the free acid present may be directly titrated with a standard solution of potassium hydroxide.

Iron, in the ferrous condition, is estimated by titration with decinormal potassium permanganate, and total iron by means of standard titanous or stannous chloride solution. If the quantity of iron present be very small, it is determined colorimetrically (v. ALUMS).

Several basic aluminium sulphates have been prepared. The compound $Al_2O_3,2SO_3,12H_2O$ is obtained by heating a solution of aluminium sulphate with zinc, or by dissolving in it the calculated quantity of aluminium hydrate. Spence and Sons, Limited (D. R. P. 1903, 167419), prepare a basic sulphate of similar composition by heating sulphuric acid under pressure with 15 to 30 p.c. more alumina than is required for the formation of the normal salt. The solution is then treated with sufficient chalk or lime to raise the basicity by 20 to 28 p.c. The strongly basic solution is rapidly filtered and concentrated in vacuó until its density reaches 1·45. On cooling with agitation, a magma of crystals is formed and is separated by suitable means from the mother liquor which contains normal aluminium sulphate (compare also Eng. Pat. 1902, 25683, and Fr. Pat. 1903, 331836).

ALUMINIUM BRONZE v. ALUMINIUM.

ALUMS. This generic name is given to an important group of double salts of the general type $R_2SO_4,R'_2O_3(SO_3)_3,24H_2O$, where R is a monovalent metal or basic radicle such as potassium, sodium, ammonium, &c., and R'_2O_3 is a sesquioxide such as that of aluminium, iron, chromium, or manganese. They are all soluble in water, and crystallise therefrom with twenty-four molecules of water, in forms belonging to the regular system, usually octahedra or cubes.

The alums which contain the sesquioxide of alumina will alone be considered here, and of these the most important are the potassium, sodium, and ammonium compounds.

'Selenic alums' have been prepared, in which sulphuric acid is replaced by selenic acid.

Potassium alum, *Potash alum*

$$K_2SO_4,Al_2O_3(SO_3)_3,24H_2O.$$
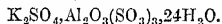
This salt is found in nature as *kalinite*, in the form of fibrous crystals or as an efflorescence on aluminous minerals, and occasionally also in octahedra, at Whitby, Campsie, &c. In the Solfatara near Naples, and the islands of Volcano and Milo, it occurs in larger quantities, being formed by the action of volcanic gases upon felspathic trachyte.

Of greater importance is the mineral *alunite* or *alumstone*, which is a double salt of potassium sulphate and basic aluminium sulphate, having the composition $K_2SO_4,Al_2(SO_4)_3,2Al_2(OH)_6$; it is found at La Tolfa near Civita Vecchia; at Montioni in the Duchy of Piombino; at

Mursaly, Munkaet, and Tokay in Hungary; in the islands of Milo, Argentino, and Nipoglio (Grecian Archipelago); at Puy-de-Sancy and Madriat (Auvergne); at Samsoun in Asia Minor; and in Australia. An 'alum mountain,' composed of this mineral, is reported to exist in China, and is stated to be nearly 1900 feet high and to have a circumference at its base of about ten miles (U. S. Cons. Report, 1903).

The manufacture of alum is of great antiquity. In the time of Pliny alum was in use as a mordant for the production of bright colours, and was even tested by means of the *tannin* in pomegranate juice to ascertain its purity. It was prepared in the thirteenth century at Smyrna from alum rock, and since the fifteenth century has been largely produced at La Tolfa from the same substance.

Its preparation from pyritic shale has long been known, together with the fact that the presence of an alkali was necessary to induce crystallisation, but, until proved in 1797 by Chaptal and Vauquelin, the essential presence of alkali in the crystals was not recognised.

Very pure alum is prepared in small quantities at Solfatara. The natural alum found there is digested with water in large wooden vats under cover, and maintained at about 40° by the natural heat of the soil. The solution is decanted and crystallised. A second crystallisation produces extremely pure alum.

Production of alum from alunite.—The preparation of alum from alunite is an industry which dates from very early times. Of Oriental origin, it appears to have been introduced into Europe in the thirteenth century, and during the fifteenth century several alum works were established. Amongst these may be mentioned the celebrated works at La Tolfa near Civita Vecchia, a district in which alum manufacture still ranks as an important industry.

The outline of the La Tolfa process given below is of historical interest. The mineral, broken into lumps of moderate size, is calcined at a low red heat, either in heaps or in kilns. The operation requires to be carefully performed, and is stopped as soon as the mineral begins to evolve acid fumes. The calcination occupies about six hours and results in a loss in weight amounting to about 33 p.c., chiefly due to the expulsion of water; at the same time the basic sulphate is decomposed, yielding alum and insoluble alumina. The roasted mass is transferred to brickwork bins and exposed to the air for several months, during which time it is occasionally moistened. The resulting sludge is lixiviated with water at 70°, and the clear decanted liquor concentrated. The crystals of alum which separate on cooling are cubic and have a reddish tinge owing to the presence of suspended ferric oxide; this may be removed by recrystallisation. The amount of soluble iron present is stated to be less than 0·005 p.c. The product, known as Roman alum, was in former times highly valued on account of its great purity.

In the modern process, employed on the Continent, the alunite is calcined at a higher temperature and the product treated with sulphuric acid, whereby aluminium sulphate is formed from the excess of alumina, and passes into solution together with the alum. The

latter is either crystallised out, and the more soluble aluminium sulphate recovered as such from the mother liquors, or sufficient potassium sulphate is added to convert the whole of the aluminium sulphate into alum.

According to C. Schwartz (Ber. 17, 2887), the best temperature for the roasting is 500°, and the acid used should have a density between 1·297 and 1·530. L. Geschwind (Manufacture of Alum and the Sulphates of Alumina and Iron, 1901), however, states that in France a temperature of about 1000° is employed.

Formerly, the greater portion of the alum manufactured in England was prepared from alum shale (alum ore), alum schist, and similar minerals, which occur in large quantities at Whitby in Yorkshire, Hurlet and Campsie in Scotland, in Sweden, Norway, Belgium, and in several parts of Thuringia, Westphalia. &c. These minerals are mixtures of aluminium silicate, iron pyrites, and bituminous substances ; the iron pyrites is principally present in the aluminous schists as a fine black powder, disseminated throughout the mass, and not distinguishable to the eye. The rapid oxidation of these minerals under atmospheric influences or heat is due to this state of fine division.

Aluminous earths are dark brown, friable, porous masses without structure, and contain less silica than the schists. They usually occur in layers with lignite.

Production of alum from aluminous shale.— The more earthy shales are porous, and if piled in heaps in the open air and occasionally moistened undergo spontaneous oxidation, with the formation of sulphates of iron and aluminium. Usually they require roasting, and when not sufficiently bituminous for combustion, are first mixed with fuel.

The coarsely broken shale is built up with alternate layers of coal into heaps, which are ignited. As the mass burns, fresh quantities of the mineral are added, until a sufficient mass of material has been accumulated. By pumping water over the surface at intervals the temperature is regulated to a degree suitable for rendering the decomposition as complete as possible. Too high a temperature is to be avoided, as it results in the loss of sulphur dioxide and the formation of a slag. During the combustion of the shale the pyrites is decomposed, giving up a portion of its sulphur, which is converted by burning into sulphur dioxide, and this in conjunction with atmospheric oxygen attacks the clay, forming aluminium sulphate. The calcined mass is allowed to remain exposed to the air for a considerable period, during which a further absorption of oxygen takes place, resulting in the conversion of the lower sulphide of iron into ferrous sulphate and ferric oxide.

Lixiviation.—This operation is carried out in large lead-lined boxes with perforated bottoms, the filtering bed being formed of timber topped with brushwood. A layer of the roasted mineral about 13 inches deep, is introduced and its extraction is effected, first with the mother liquor from the alum crystallising pans, and later with pure water, the liquid in each case being left overnight in contact with the material.

The exhausted mineral still contains a considerable amount of alumina and sulphuric acid. The liquors, which have a density of 1·09 to 1·15, are run into settling tanks and allowed to deposit calcium sulphate, ferric oxide, and other suspended impurities, and are then removed for concentration. The method adopted for this purpose varies according to the nature of the mineral under treatment. In the case of shales from Hurlet and Campsie the concentration is effected by surface evaporation in a reverberatory furnace.

The bed is of stone, coated with well-rammed clay, 4 or 6 feet wide, 2 or 3 feet deep, 30 or 40 feet long. It is filled to the brim with strong liquor, and the flame and hot air from the fire carried over it. As evaporation proceeds, more liquor is added until the proper concentration is reached. It is then run into leaden pans, concentrated to about 1·4 sp.gr. and conveyed to a precipitating cistern containing the requisite quantity of dry potassium chloride ; the liquid is well agitated and the chloride soon dissolves. In about 5 days the liquor is drained from the large crystals, which are washed and recrystallised.

The Whitby shales differ from those at Hurlet, in that they contain a considerable quantity of magnesia which passes into the extract in the form of magnesium sulphate. In this case surface evaporation is not satisfactory on account of the formation of a crust of this salt which retards evaporation. The evaporation of the liquor is carried out, therefore, in leaden vessels, until a sp.gr. of 1·125 to 1·137 is reached, after which the solution is allowed to stand until clear. The concentration is continued up to sp.gr. 1·25, at which stage a sample of the liquor is withdrawn and the percentage content of aluminium sulphate determined. After further evaporation to a density of 1·4 to 1·5, the hot liquor is run into a precipitating tank and mixed with a saturated solution of the calculated quantity of potassium chloride or sulphate, the whole being kept in constant agitation to induce the formation of small crystals (alum meal).

When much ferric sulphate is present in the solution, the addition of potassium sulphate would produce iron alum, isomorphous with ordinary alum, which would crystallise out and contaminate the product. The use of potassium chloride prevents this, by producing the easily soluble ferric chloride, while ferrous salts are converted into the equally soluble ferrous chloride, an equivalent amount of potassium sulphate being formed at the same time. Chloride of potassium is generally employed in preference to the sulphate, whenever sufficient iron sulphate is present to supply the requisite amount of sulphuric acid for the formation of alum ; its greater solubility is also in its favour. Too much chloride should be carefully avoided, for after the iron sulphates have been decomposed, the aluminium sulphate is itself attacked, with the production of the very soluble chloride, which is lost.

The *alum meal,* consisting of small brownish crystals, is drained and washed twice with cold water. The adhering mother liquor, containing much iron, is thus removed, and the meal is left nearly pure. The final purification is effected by dissolving in a minimum quantity of boiling water and allowing the solution to stand for about eight days in casks furnished with movable

At the end of this period the staves are removed, the block of crystals is pierced, the mother liquor drained off and employed for dissolving fresh quantities of meal.

The mother liquor from the alum meal has a sp.gr. of about 1·4; it contains sulphate or chloride of iron, magnesium sulphate, &c., and will yield more alum on evaporation. In a final evaporation it yields ferrous sulphate in fine green crystals. When iron is present in large quantity, the liquors are evaporated and the ferrous sulphate crystallised out before the addition of the potassium salt. In this case the iron salt is less pure and less soluble, but the alum subsequently produced contains less iron.

Formerly, potassium alum was alone produced. In 1845, however, the potassium sulphate was replaced by the ammonium sulphate produced from the then waste liquors from gas works, yielding ammonium alum. This great improvement was introduced by the late Peter Spence; his method was soon generally adopted both in England and on the Continent.

Another great advance was made by Spence in 1845 in the manufacture, by the treatment of the refuse shale underlying the coal-seams of South Lancashire. This shale contains from 5 to 10 p.c. of carbonaceous matter. It is piled upon rows of loosely placed bricks (to allow a free passage to the air) in heaps 4 or 5 feet high and 20 feet long. The combustion is started with a little fuel, but the shale contains sufficient combustible matter to continue burning. The calcination is performed slowly at a heat below redness. In about 10 days the roasting is completed, and the material has become soft, porous, and light red, whilst the alumina contained in it has become anhydrous and soluble in sulphuric acid. Too high a temperature, however, partially vitrifies it, in which case it is only slowly attacked by acid. Charges of 20 tons are placed in large covered pans 40 feet long, 10 feet wide, and 3 feet deep, lined with lead, and are digested for about 48 hours with sulphuric acid (of sp.gr. 1·35) at 110°, the temperature being maintained by fires beneath the boilers. Formerly ammonia was forced into the liquid from a boiler containing gas liquor; ammonium sulphate was thus produced, with considerable rise of temperature, and combined with the aluminium sulphate forming ammonium alum. The solution of alum so produced is run into cisterns 29 feet by 17 feet, and 1¾ feet deep, in which it is kept in constant agitation. In about 14 hours the small crystals so formed are drained, washed with some mother liquor from 'block alum,' and dissolved by a process known as 'rocking' for the production of pure block alum. For this purpose they are introduced into a hopper, at the bottom of which they encounter a current of steam at a pressure of 20 lbs. per sq. inch, both steam and crystals being supplied in such proportions that all the crystals are dissolved, while no steam is wasted. In this manner 4 tons of crystals may be dissolved in 30 or 40 minutes. The solution is run into a leaden tank, and, after a time, treated with a small quantity of size, which precipitates a quantity of insoluble matter. The clear liquid is next run into tubs about 6 feet high and 6 feet wide, tapering upwards, with movable lead-lined staves. After

some days the staves are removed and a hole is bored in the mass of crystals for the removal of the liquor. Each block weighs about 3 tons, while the mother liquor contains about 1 ton.

To produce 1 ton of ammonium alum by this method on an average about 15 cwts. of the shale is required.

A great advantage of this process is the speed with which the crude material is converted into marketable alum. By the old process twelve months was required for this conversion, whilst by Spence's process the whole operation is performed in one month. For this process Spence was awarded the medal for alum manufacture at the Exhibition of 1862, at which date he manufactured 150 tons of alum weekly, over one-half the total production of England (v. Hofmann's Report on Chemical Processes at the Exhibition of 1862, p. 62, and J. Carter Bell, Chem. News, 12, 221).

Alum is also produced by the addition of potassium sulphate to aluminium sulphate, prepared by any of the processes already described. It is prepared in great purity from the sulphate produced from cryolite; 1 ton of cryolite produces 3 tons of alum (v. Sodium aluminate).

Many other processes have been proposed and used for the preparation of alum.

Spence, in 1870 (Eng. Pat. 1676), patented a method of preparing alum from mineral phosphates, especially that from Redonda near Antigua, which contains 26·1 p.c. of alumina as phosphate with ferric oxide and silica. It is calcined at a red heat to render it porous, powdered, and digested with sulphuric acid of sp.gr. 1·6 in quantity proportional to the amount of alumina, in lead-lined vessels, heated by steam. The liquid is concentrated to a density of 1·45, and treated with the requisite amount of potassium sulphate to convert the whole of the alumina into alum. Phosphate containing 20 p.c. of alumina yields about 1¼ times its weight of alum, from which, however, the last traces of phosphoric acid are removed with difficulty. The phosphoric acid in the mother liquors is valuable as a manure.

Methods have frequently been proposed for the preparation of alum from felspar. Ordinary felspar contains both potassium and aluminium combined with silica in larger proportions than are contained in alum; the problem to be solved is the substitution of sulphuric acid for silica. A method adopted by Turner, said to have been originated by Sprengel, consisted in the ignition of a mixture of one part of the powdered mineral with one part of potassium bisulphate until fused; one part of sodium carbonate was then added, and the whole again fused. The mass was boiled with water and the insoluble double silicate remaining was decomposed by hot sulphuric acid of sp.gr. 1·20, and the alum crystallised out. On account of the high temperature required, this process was not successful.

At the present time the bulk of the alum manufactured in England is prepared either from shale or from the aluminium sulphate derived from bauxite or china clay.

For the more delicate dyes the alum used must be of extreme purity. Samples containing even less than 0·001 p.c. of iron may be unsuitable for certain purposes. The percentage of iron in alum or in aluminium sulphate is usually

determined by means of a solution of ammonium thiocyanate standardised with iron alum. Many precautions are necessary in performing the analysis (*v.* Tatlock, J. Soc. Chem. Ind. 1887, 276 ; G. Lunge, Mon. Sci. 1897, 160).

Potassium alum crystallises with 24 molecules of water, in crystals belonging to the cubic system, usually in large colourless octahedra of sp.gr. 1·751 (Retgers, Zeitsch. physikal. Chem. 3, 289 ; J. B. 1889, 148).

De Boisbaudran has also obtained it crystallised with hemihedral faces of the tetrahedron. The crystalline form is affected by the presence of other substances in solution, and by the temperature. When formed at ordinary temperatures in the presence of basic alum, the crystals are cubes, frequently dull on the surface from the presence of the basic salt ; for this reason Roman alum usually forms cubes. At 40°, even in presence of basic salts, octahedra are produced.

Potassium alum possesses the property of crystallising with hydrogen peroxide (Willstätter, Ber. 36, [1903] 1828).

According to Poggiale (Ann. Chim. Phys. [3] 8, 467), the solubility of potassium alum and of ammonium alum is as follows :—

100 parts water dissolve :

°C.	Crystallised Potassium alum	Crystallised Ammonium alum
0	3·9	5·2
10	9·5	9·1
20	15·1	13·6
30	22·0	19·3
40	30·9	27·3
50	44·1	36·5
60	66·6	51·3
70	90·7	72·0
80	134·5	103·0
90	209·3	187·8
100	357·5	421·9

Conductivity determinations, made on alum solutions of different concentrations, indicate that even at moderate dilutions the alum is resolved into its component salts.

Potassium alum possesses a sweetish astringent taste and a strongly acid reaction. The aqueous solution decomposes when heated, with precipitation of a basic alum, especially when dilute. For this reason a small quantity, not sufficient to be distinguished by taste, is frequently added to impure water. The gelatinous precipitate carries with it the colouring matter and most of the organic impurities, producing a slimy deposit.

Alum is almost insoluble in a saturated solution of aluminium sulphate, and is quite insoluble in alcohol. On exposure to air, the crystals become white on the surface. This change is due, not to the loss of water, but to the absorption of ammonia from the air, with formation of a basic salt. Below 30° they lose no water ; at 42° they evolve 11 molecules (Juttke, Chem. Zentr. 18, 777). In a closed vessel over sulphuric acid they lose 18 molecules at 61° (Graham) and become slowly anhydrous at 100°, more rapidly in a current of air. Alum melts in its water of crystallisation at 92·5°, and when heated to dull redness is converted into a porous

friable mass, slowly soluble in water, known as 'burnt alum.' At a white heat alumina and potassium sulphate alone remain.

When burnt alum is mixed with one-third its weight of carbon and heated to redness, the residue is spontaneously inflammable on account of the presence of finely divided potassium sulphide, and is known as Homberg's pyrophorus. By fusing alumina with potassium bisulphate and digesting the mass in warm water, anhydrous potassium alum may be obtained in crystals of which 5 parts are soluble in 100 of water at 10° and 74·5 parts at 100° (Salm-Horstmar, J. pr. Chem. 52, 319).

On the addition of caustic soda or sodium carbonate to a solution of alum until the precipitate at first produced is only just redissolved on agitation, *i.e.* when two-thirds of the acid has been neutralised, the solution contains a neutral basic alum, known as *neutral alum*, together with sodium sulphate. This solution, on account of the ease with which it gives up its excess of alumina to the fabric, is used by dyers as a mordant. Commercial potassium alum is frequently mixed with ammonium alum.

Alum is extensively used as a mordant in the dyeing industries, and in the production of other aluminium mordants such as the acetate, sulphoacetate, &c., employed in dyeing and printing and for shower-proofing fabrics. The alum used for dyeing with alizarin red must be free from iron, otherwise dull shades are produced. It is also employed in the manufacture of lake pigments, in the dressing of skins (' tawing ') to produce white leather, in sizing paper, and in the production of fireproofing materials. In most of its applications, however, it is being replaced by aluminium sulphate, the use of which is considerably more economical.

Sodium alum, *Soda alum*

$$Na_2SO_4,Al_2O_2(SO_3)_3,24H_2O.$$
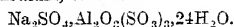
Occurs as *mendozite* in S. America and in Japan (Divers, Chem. News, 44, 218).

This alum was prepared by Zellner in 1816, by the spontaneous evaporation of a solution containing the sulphates of sodium and aluminium. Its existence, disputed by Ostwald, has been established by Wadmore (Chem. Soc. Proc. 21, 150 ; C.-B. 1905, 11, 18), who from a solution of the mixed sulphates obtained octahedral crystals having the above composition. From a hot concentrated solution it is deposited on cooling as a pasty mass which slowly becomes crystalline. Contrary to the statement frequently made, the crystals do not appreciably effloresce in the air.

Technically, sodium alum may be prepared in the following manner :—To a solution of aluminium sulphate containing 675 grams of the crystalline salt per litre, and maintained at a temperature of 50° to 60°, is added a solution of sodium sulphate containing 146 grams of the anhydrous salt per litre, until the liquid attains a density of 1·35 ; crystals of sodium alum separate on cooling. The crystallisation should be effected at a temperature between 10° and 25° ; at 28° the formation of crystals proceeds very slowly, whilst below 10° separation of sodium sulphate occurs (Augé, D. R. P. 1899, 50323 ; J. 1890, 2635).

Messrs. F. M., D. D., and H. Spence (Eng. Pat. 1900, 5644) prepare a solution of sodium sulphate saturated at 40° to 50°, which is allowed to cool during agitation until a considerable proportion of decahydrated crystals have separated. The mixture of liquid and crystals is then run into a solution of aluminium sulphate containing the solid salt in suspension. There is thus obtained a large crop of well-defined soda alum crystals. Alternatively, the solid aluminium sulphate may be added to a suitable solution of sodium sulphate or chloride, in which either salt may be suspended in the solid state.

Sodium alum is much more soluble at ordinary temperatures than potassium or ammonium alum, in consequence of which it is more difficult to purify from iron. On account of the lower cost of sodium salts, it would be largely used in place of other and more expensive alums, if it could be easily purified by crystallisation (see Eng. Pat. 1881, 5650).

Sodium alum crystallises with 24 molecules of water in regular octahedra, having a sp.gr. of 1·667 (Soret). At 10·6° 100 parts of water dissolve 107·11 parts of the alum (Wadmore); according to Ure, the solution saturated at 15·5° contains 110 parts of the alum in 100 of water, and has a density of 1·296. Sodium alum is insoluble in alcohol.

Ammonium alum

$$(NH_4)_2SO_4,Al_2O_3(SO_3)_3,24H_2O$$
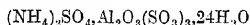
occurs as *Tschermigite* in Bohemia, and in the crater of Mount Etna.

Its preparation is analogous to that of potassium alum, a solution of aluminium sulphate, prepared by any of the methods already described, being treated with the equivalent quantity of ammonium sulphate, and the alum separated and purified by crystallisation.

Ammonium alum crystallises with 24 molecules of water in regular octahedra, having a conchoidal fracture and a density of 1·631 (Soret). At ordinary temperatures it is less soluble in water than potassium alum (*v.* Table of solubilities, under Potassium alum). The saturated solution boils at 110·6°, and contains 207·7 parts of the alum to 100 parts of water (Mulder). When heated the crystals swell up and form a porous mass, losing water and sulphuric acid ; at a high temperature alumina alone remains. This serves as a useful method for the production of very pure alumina.

In its general properties and uses, ammonium alum closely resembles the corresponding potassium compound.

Aluminium sulphite $Al_2O_3(SO_2)_3$.

The bisulphite has been used by Becker (Dingl. poly. J. 257, 300), Suchomel (J. Soc. Chem. Ind. 1887, 143) and others, for the purification of beet sugars. Becker prepares for this purpose a solution of sp.gr. 1·167 containing 4·37 p.c. alumina and 13·9 p.c. sulphurous oxide, by dissolving the hydrated oxide in sulphurous acid.

Aluminium phosphates. As hydrated phosphate, aluminium occurs in the *turquoise*, and enters into the composition of *wavellite, lazulite* and *gibbsite*. It is found in considerable quantity in mineral phosphates, as in the Redonda phosphates which have been used for the preparation of alum and for fertilisers (*v.* ALUMS; MANURES). A massive stony variety

is found on the island of Anguilla in the West Indies.

Aluminium thiocyanate or **sulphocyanate** has been proposed as a substitute for aluminium acetate for alizarin, steam reds, &c. ; the colours produced are said to be especially permanent (*v.* Storch and Ströbel, Dingl. poly. J. 241, 464 ; and Gottlieb Stein, Dingl. poly. J. 250, 36).

Lauber and Haussmann (Dingl. poly. J. 245, 306) recommend the following method of preparation : 5 kilos. aluminium sulphate are dissolved in 5 litres boiling water, 250 grams of chalk are added, followed by 11·5 litres of crude calcium thiocyanate solution of 30°Tw., and the whole well stirred and allowed to settle. The clear liquid is ready for use.

Aluminium permanganate *v.* MANGANESE.

Aluminium silicates. These compounds are exceedingly numerous and important. As an anhydrous silicate, with silicate of iron, calcium, magnesium, &c., aluminium occurs in the varieties of *garnet*, crystallising in the regular system. As silicate of aluminium, calcium, and sodium it is found in *lapis-lazuli*, which was formerly used as *ultramarine*. It is now replaced by artificial ultramarine (*v.* ULTRAMARINE). As silicate of aluminium, combined with potassium, iron, and magnesium, it occurs in the *micas*. As double silicate of aluminium, potassium, sodium, magnesium, or calcium, it forms the varieties of *felspar* which occur in immense quantities in eruptive rocks. By the decomposition of felspar by the carbonic acid in the atmosphere and in rain or spring water, the alkaline compounds are removed, leaving clay of more or less purity (*v.* CLAY), which, under pressure, becomes hardened and laminated, forming *shale*, and finally *slate* (*q.v.*). Many of the silicates of aluminium are of great importance, and of the widest application. The more important of them are specially considered under their applications (*v.* POTTERY : PORCELAIN).

Aluminium acetate. *Red liquor* (*v.* Aluminium acetates*, art.* ACETIC ACID).

The compounds of aluminium with the higher fatty acids are used for increasing the viscosity of mineral lubricating oils, under the names ' oil pulp ' and ' fluid gelatin ' (L. Marquardt, Zeitsch. anal. Chem. 25, 159).

Aluminium oleate is a soft white, putty-like substance, of great tenacity, insoluble in water, soluble in ether and petroleum. A mixture of oleate, palmitate, and other fatty salts is produced from whale, cotton-seed, and similar oils by saponification with soda and addition of the sodium salt so produced to a solution of alum. The gummy precipitate is known as ' oil pulp,' and is dissolved in 4 or 5 parts of mineral oil to form a ' thickener ' for addition to the lubricator. A sample of oil pulp resembling thick gelatin had a sp.gr. of 0·921, and contained 6 p.c. alumina combined with 30 p.c. fatty acids, together with 15 p.c. lard oil, and 48 p.c. paraffin oil (Oil and Colourman's Journ. 4, 403).

Aluminium palmitate is a constituent of oil pulp. It may be prepared in the same manner as the oleate, from palm oil. It forms a resinous, elastic, inodorous, neutral substance, insoluble in water, but readily soluble in petroleum and turpentine. K. Lieber (Dingl. poly. J. 246, 155) recommends the use of the latter solution as a varnish. It imparts a glossy appearance to

paper, leather, &c., and renders them waterproof without affecting their elasticity.　G. H. B.

ALUMNOL *v.* SYNTHETIC DRUGS.

ALUM-SHALE. A kind of shale or slate containing disseminated iron pyrites, which, on prolonged exposure to the weather, gives aluminium sulphate, owing to the action of sulphuric acid (from the decomposition of the iron pyrites) on the clayey material. The heaps of weathered shale are leached with water, and to the solution of aluminium sulphate and sulphuric acid so obtained potashes are added. The alum obtained by the evaporation of this solution is purified by recrystallisation. The alum-shales of Liassic age on the coast of Yorkshire, in the neighbourhood of Whitby, have been largely worked by this method since the time of Queen Elizabeth, but now the industry has become extinct. Alum-shales in the coal-measures of the West Riding of Yorkshire are, however, still worked to a small extent (*v. Alums*, art. ALUMINIUM).　L. J. S.

ALUNDUM. An abrasive manufactured at Niagara Falls from fused bauxite (*v.* ABRASIVES and BAUXITE).

ALUNITE or **ALUM - STONE.** Hydrated basic sulphate of aluminium and potassium $KAl_3(SO_4)_2(OH)_6$, usually found as white, compact, granular masses, somewhat resembling limestone in appearance. It mostly occurs in connection with volcanic rocks, having been formed by the action of solfataric vapours on such rocks. In some cases, however, it may have been formed by the action of decomposing iron-pyrites on clay. Extensive deposits are met with at Tolfa near Rome, in Tuscany and Hungary, and at Bulladelah in New South Wales. Alum is obtained from it by repeatedly roasting and lixiviating, the yield being from 60 to 80 p.c. In Hungary the harder and more compact varieties have been used for millstones.
　　　　　　　　　　　　　　　　L. J. S.

ALUNOGEN. Hydrated aluminium sulphate $Al_2(SO_4)_3,18H_2O$, occurring as a white, delicately fibrous efflorescence on shale and other rocks. It has been formed by the action on the aluminous rock of the products of decomposition of iron pyrites. A trace of iron sulphate is often present, imparting a yellowish or reddish colour to the mineral.　　　　　L. J. S.

ALVA or **ALFA** *v.* ESPARTO.

ALVELOS. A name applied to the *Euphorbia heterodoxa* (Muell.), growing in Brazil, the juice of which has been used as a cure for cancer (Pharm. J. [3] 15, 614).

ALYPIN. Trade name for *benzoyltetramethyl-diamino-ethyldimethylcarbinol hydrochloride.* Employed as an anaesthetic and as a remedy for vomiting and in the treatment of diseases of the upper respiratory passages and of the organ of hearing. Used also in veterinary practice in place of cocaine.

It occurs in crystals, m.p. 169°, sol. in water, forming a neutral solution. Aqueous solutions may be sterilised without undergoing decomposition by boiling from 5 to 10 minutes (Neustätter, Pharm. J. 1905, 869).

(For distinctive reactions, *v.* Lemaire, Rep. Pharm. 1906, 18, 385.) (*v.* SYNTHETIC DRUGS.)

AMADOU or **GERMAN TINDER.** (*Amadou*, Fr.; *Zunderschwamm*, Ger.) A spongy combustible substance, prepared from a species of fungus, *Fomes (Polyporus) igniarius*, the ' false ' tinder-fungus, which grows on the trunks of the oak, but also on alder, willow, and various other trees. It must be plucked in the months of August and September. It may also be prepared from *Fomes (Polyporus) fomentarius*, the true tinder-fungus, also indigenous, found especially on the beech, elm, and various fruit trees. It was formerly used in surgery, and has hence been called surgeons' agaric. Amadou is prepared by removing the outer rind and carefully separating the yellow-brown spongy substance which lies within it. This substance is cut into thin slices, and beaten with a mallet to soften it, till it can be easily pulled asunder between the fingers. In this state it is useful in surgery. To convert it into tinder, it is boiled in a strong solution of nitre, dried, beaten anew, and put a second time into the solution. Sometimes, to render it very inflammable, it is imbued with gunpowder, whence the distinction of ' black ' and ' brown ' amadou.

AMALGAM. An alloy of mercury with some other metal or metals.

There are four general methods for preparing —

1. Metallic mercury is brought into contact with the other metal, either in the solid or in a finely divided state at the ordinary or at a higher temperature. In this way amalgams of antimony, arsenic, bismuth, cadmium, magnesium, potassium, silver, sodium, tellurium, thorium, tin, zinc, and lead may be obtained.

2. Mercury is brought into contact with a saturated solution of a salt of the metal, when part of the mercury goes into solution and the remainder combines with the liberated metal; or better still, zinc or sodium amalgam is employed, when the zinc or sodium displaces the metal in the solution. By this method amalgams of bismuth, calcium, chromium, iridium, iron, magnesium, manganese, osmium, palladium, and strontium may be prepared by using sodium amalgam, and cobalt and nickel by using zinc amalgam (Moissan, Compt. rend. 1879; Chem. News, 39, 84).

3. The metal to be amalgamated is placed in a solution of a mercury salt; copper may be amalgamated by this process.

4. The metal is placed in contact with mercury and dilute acid; this is the method usually employed in amalgamating zinc. Iron, aluminium, palladium, nickel, and cobalt may be made to combine with mercury by this process if they be placed in contact with a stick of zinc (Casamajor, Chem. News, 34, 36; Arch. Pharm. [3] 11, 64; Chem. Soc. Trans. [2] 34, 474).

Amalgams are also formed when mercury is used as the cathode in the electrolysis of salt solutions; a number of metals can thus be obtained as amalgams, although they cannot be obtained directly in the free state by the electrolysis of aqueous solutions.

The combination of sodium with mercury by method 1 takes place with great energy, heat and light being produced. It is best prepared by combining a small portion of the mercury with the sodium, and then adding the remainder to the amalgam.

Native amalgams are found in various parts of the world. The following table contains the analyses of a few :—

Ag	Hg	Au	Fe_2O_3	CaO	AgCl	Fe	Zn	Pb	$CaCO_3$	Cu	Insol. and loss	Locality	Analyst and reference
75·900	23·065	—	—								0·490	Kongsberg, Norway.	Flight, Phil. Mag. [5] 9, 146.
92·454	7·195	—	0·033	0·055	0·088						1·328	Moschellandsberg, Palatinate.	Klaproth, Ure 1.
36·0	64·0	—	—									"	"
25·0	73·3	—	—									Allemont, Dauphiné.	Heyer, id.
27·5	72·5	—	—										Cordier, ib.
46·30	51·12	—	—				0·18	tr.	tr.	0·21		Salagrube, Sweden.	Nordström, J. 35, 1, 521.
56·70	43·27	—	—							tr.		Friedrichssegen.—Mine.	Weiss, J. 36, 1828; Z. geol. Ges. 34, 817.
—	60·98 to 58·37	39·02 to 41·63	—									Mariposa, California.	Ure.
5·00	57·40	38·39	—									Choco, New Grenada.	Schneider. Ure.

Gold and silver in the metallic state can be extracted from their ores by grinding the ores and making them pass through mercury, although this process is now largely replaced by the modern cyaniding methods. (For details, v. these metals; and May, J. Soc. Chem. Ind. 4, 352; Moon, id. 4, 678; Miller, id. 4, 122; Whitehead, id. 4, 503; Fisher and Waber, id. 4, 351; Barker, Dingl. poly. J. 251, 32; Body, id. 252, 33; Molloy, id. 254, 210; Bonnet, id. 254, 297; Cassel, id. 257, 286; Jordan, id. 258, 163; Hollick, id. 258, 168.) When the mercury has taken up a quantity of gold, the amalgam is squeezed through chamois leather, when the greater portion of the gold is left, combined with a little mercury, as a pasty mass. Kazantseff (Bull. Soc. chim. [2] 30, 20; Chem. Soc. Trans. [2] 34, 937) finds that the mercury which escapes contains at ordinary temperatures 0·126 p.c. of gold, at 0° 0·110 p.c., and at 100° 0·650 p.c., thus behaving like an aqueous solution.

Berthelot found that the solution of definite amalgams in different quantities of mercury, like the solution of salts in water, absorbs a constant amount of heat: thus the heat of solution of an amalgam of which the composition corresponds with the formula $Hg_{24}K$ in four times its weight of mercury is −8·0 kil. deg. of heat, and in twenty times −9·0 kil. deg. (Compt. rend. 89, 465; Chem. Soc. Abstr. 38, 1).

According to Berthelot, the maximum heats of formation for amalgams of potassium and sodium are 34·2 and 21·1, corresponding with crystalline amalgams containing 1·6 p.c. of potassium, and 2 p.c. of sodium respectively. In these amalgams the relative affinities of the free alkali metals are inverted: this explains Kraut's and Popp's observation that sodium displaces potassium when potassium hydroxide is treated with sodium amalgam, the final result being the formation of an amalgam of composition $Hg_{24}Na$ (Compt. rend. 88, 1335).

The views formerly held on the constitution of amalgams and particularly on the existence of definite amalgams of the nature of chemical compounds of mercury and the alloyed metal, have been profoundly modified by the study of these bodies by the methods of metallography (v. METALLOGRAPHY). The amalgams are found to be strictly analogous to other alloys, but their peculiar behaviour arises from the fact that they are frequently met with in a range of temperature which lies between the commencement of solidification and final complete crystallisation. It has been shown that a number of supposed compounds, of which the existence had been assumed on the ground that amalgams representing them took the form of homogeneous crystalline bodies, are not true compounds, whilst definite compounds of different composition have been found. Thus, in the case of sodium and potassium amalgams, the compounds Hg_4Na, Hg_2Na, $HgNa$, Hg_2Na_3, Hg_3Na_5, and Hg_2K, HgK, Hg_3K, Hg_5K_2, and Hg_5K, have been recognised (Schüller, Zeitsch. anorg. Chem. 1904, 40, 385; Kurnakoff, ibid. 1900, 23, 439; Jaenecke, Zeitsch. physical. Chem. 1907, 58, 245).

The amalgams of bismuth, zinc, tin, and thallium are found not to contain any definite compounds (Puschin, Zeitsch. anorg. Chem. 1903, 36, 201; Heteren, ibid. 1904, 42, 129; Kurnakoff and Puschin, ibid. 1903, 30, 86).

'Ammonium amalgam' is prepared by acting on a saturated solution of ammonium chloride with sodium amalgam; the amalgam thus obtained soon breaks up into mercury, and ammonia and hydrogen gases. According to Wetherill (Amer. J. Sci. [2] 50, 160), this compound is not a true amalgam, as when an ammoniacal solution is electrolysed, the negative pole being a spongy plate impregnated with mercury, no amalgam is formed. Landolt (Zeitsch. f. Chem. [2] 5, 429) draws attention to the fact that ammonium amalgam does not reduce solutions of silver nitrate, ferric chloride, or cupric sulphate, as do sodium and potassium amalgams.

Seeley (Chem. News, 21, 265) has shown that on submitting ammonium amalgam to pressure, its volume diminishes in the same way that gases do, and hence he considers that the ammonia and hydrogen exist in the amalgam as gas, and that the spongy mass is only a froth of mercury inclosing these gases.

Gellatlin (Zeitsch. f. Chem. [2] 5, 607) asserts that when ammonium amalgam, free from sodium, is placed in contact with phosphorus, phosphoretted hydrogen is evolved, and he infers that the hydrogen must be in the nascent state.

Pfeil and Lippmann (Compt. rend. 62, 426) state that trimethylamine hydrochloride also forms a spongy amalgam which quickly decomposes with evolution of hydrogen and formation

of trimethylamine; saturated solutions of the hydrochlorides of aniline, coniine, morphine, and quinine give off hydrogen only.

Electrical amalgam is made by melting together 1 part of zinc and 1 part of tin, and then adding 3 parts of mercury. An amalgam of cadmium is used in the construction of the cadmium standard cell; this amalgam and its electrical behaviour have been studied by F. E. Smith (Phil. Mag. February, 1910).

Silvering amalgams. For metals, 1 part of silver to 8 parts of mercury; for glass, 1 part each of lead and tin, 2 parts bismuth, and 4 parts mercury. The use of amalgams for silvering has been almost completely superseded by the use—in the case of glass—of chemically deposited silver, and in the case of metals by electro-plating.

Teeth fillings. 1. Copper precipitated from copper sulphate solution with zinc, washed with sulphuric acid containing a small quantity of mercuric nitrate, and amalgamated with twice its weight of mercury (Fletcher), has the property of softening with heat and hardening again after a few hours. It is a permanent filling, as the copper salts penetrate and preserve the tooth substance. It has the objection of staining the tooth, and is only used in posterior teeth. 2. A palladium amalgam is sometimes employed, but its rapidity of setting, intense black colour, and cost are against its general use. 3. An alloy of silver 68·5, tin 25·5, gold 5, and zinc 1 p.c. (Black); or silver 69·5, tin 25·5, gold 4, and zinc 1 p.c. (Tulloch), amalgamated with mercury, is extensively employed, as it has a good edge strength, and suffers little, if any, shrinkage. The shrinkage is the greatest difficulty to overcome in order to render alloys of permanent use for teeth filling, the object being to secure such a proportion of metals that the shrinkage of one may be overcome by the expansion of another, and so obtain a watertight plug.

AMALIC ACID *v.* Alloxantin.

AMANITA MUSCARIA. *Fly agaric.* A poisonous fungus, used in Kamtschatka and Siberia as a narcotic and intoxicant, and, when steeped in milk, as a fly-poison. A narcotic organic base, *muscarine* $C_5H_{15}NO_3$, which is the hydrated aldehyde of betaine, has been isolated from it (Schmiedeberg and Harnack, J. 1876, 804).

The natural muscarine is like the artificial product in crystalline form, solubility, and composition of its platino- and auro-chlorides, and to a large extent in its physiological action, but unlike the artificial muscarine it does not induce paralysis of the intermuscular nerve-terminations in the frog, and myosis in the pupils of the eyes of birds (Nothnagel, Ber. 26, 801). It differs both in constitution and properties from anhydro- and *iso*-muscarine.

A green and red dye of composition $C_{29}H_{40}O_{10}$, and $C_{19}H_{18}O_6$ respectively, have also been isolated from it (Griffiths, Compt. rend. 130, 42).

AMARANTH *v.* Azo-colouring matters.

AMAZON-STONE. A bright-green variety of the potash-felspar microcline ($KAlSi_3O_8$). It is found in granitic rocks near Lake Ilmen in the Ural Mountains, at Pike's Peak in Colorado, and recently of very good quality in Madagascar. It is used to a limited extent as a gem-stone, and for making various small ornamental objects (*v.* Felspar). **L. J. S.**

AMBAR LIQUID *v.* Balsams.

AMBER or **SUCCINITE.** (*Bernstein*, Ger.) A fossil resin derived from the extinct conifer *Pinites succinifer* (Göppert), and found as irregular nodules in strata of Tertiary age, principally on the Prussian coast of the Baltic. The amber-bearing stratum lies partly below sea-level, and the amber washed out by the action of the waves is picked up on the sea-shore or won by dredging. Such 'strand-amber' was formerly collected farther west, as far as the coast of Holland, and isolated specimens are picked up on the east coast of England (Norfolk, Suffolk, and Essex). At the present time the bulk of Prussian or Baltic amber is obtained from pits and mines in the 'blue earth' in Samland, East Prussia. Here the production in 1907 amounted to 404,300 kilos. and in addition about 20,000 kilos was collected on the sea-shore.

Baltic amber differs from other fossil resins in containing succinic acid, which is present to the extent of 3 to 4 p.c. in perfectly transparent specimens, but reaching 8 p.c. in cloudy ('frothy') amber. It is then generally wished by the mineralogical name *succinite*, and it is the trade the tendency is to apply the name 'amber' exclusively to Baltic amber. The composition is somewhat variable, averaging C, 79 p.c.; O, 10·5 p.c.; H, 10·5 p.c.; and corresponding approximately with the formula $C_{10}H_{16}O$. Sulphur is also present (0·26 to 0·42 p.c.), and some ash, usually about 0·2 p.c., but increasing in amount if the material encloses foreign matter. Amber is, however, not a simple resin; when heated, it gives oil of amber (*q.v.*) and other products, and by the action of solvents at least four different kinds of resin can be extracted from it. According to O. Helm, Baltic amber contains 17 to 22 p.c. of a resin (m.p. 105°) soluble in alcohol; 5 to 6 p.c. of a resin (m.p. 145°) insoluble in alcohol, but soluble in ether; 7 to 9 p.c. of a resin (m.p. 175°) insoluble in alcohol and ether, but dissolving in caustic potash; and 44 to 60 p.c. of insoluble bitumen.

Baltic amber is usually pale yellow, ranging to brown or reddish-brown in colour, and it varies from perfect transparency to opacity. The varying degrees of turbidity are due to the presence of vast numbers of microscopic air-bubbles. The enclosure of insects and fragments of wood and dirt in amber is well known, and points at once to the mode of origin of the material. According to differences in colour and transparency, various trade names are applied, such as 'clear,' 'flohmig,' 'cloudy,' 'bastard,' 'osseous' or 'bone,' and 'frothy.' The sp.gr. ranges from 1·05 to 1·10 (varying with the porosity); and the hardness is 2½, being rather higher than that of most other resins, which latter can be scratched with the finger-nail. The material is brittle and breaks with a conchoidal fracture. When cut with a knife, parings are not obtained, but only powder. It can be turned on the lathe and takes a good polish, being worked with whiting and water or rotten-stone and oil, and finished by friction with a flannel. When heated, amber begins to soften at about 150°, giving a characteristic odour; it melts at 350°–375°, that is, at a higher temperature than other resins, giving dense white fumes with a peculiar aromatic odour, and causing violent coughing. When rubbed it

becomes negatively electrified (from the ancient name *electron*, for amber, the word 'electricity' is derived) ; and when rubbed vigorously it emits an aromatic odour, but does not become sticky like other resins. These characters serve to distinguish true amber from the more abundant copal ; the latter is further usually clearer, lighter in colour, and more gummy in appearance.

In the trade the material is sorted into many grades suited for various purposes. The larger pieces of better quality ('work-stone') are cut into beads and other small personal ornaments, and are largely used for making the mouthpieces of tobacco-pipes and cigar- and cigarette-holders. Smaller and impure fragments ('varnish') are melted down for the manufacture of amber varnish and lac ; but in recent years such material is largely converted by the application of heat and hydraulic pressure into blocks of *pressed amber* or 'ambroid.' About 35,000 kilos. of pressed amber is now produced annually from three times the amount of rough amber ; it is cut for ornaments and smokers' mouth-pieces. Prices (current in 1908) for rough 'work-stone' vary from 11*l.* to 10*s.* per kilo, and for smaller, inferior material ('varnish') about 5*s.* per kilo. Pressed amber fetches 4*l.* to 5*l.* per kilo. The production and the trade in amber, as well as the literature of the subject, is almost exclusively German, though the finished articles are largely made in Vienna.

Other varieties of fossil resin closely allied to amber, but regarded as distinct from Prussian or Baltic amber (succinite), are the following :—

Beckerite (E. Pieszczek, 1880), a black resin occurring with Prussian amber.

Burmite, Birmite, or Burmese amber (F. Noetling, 1893), a dark reddish-brown, amber-like resin, which has long been mined in Upper Burma and used in China. It is found in large masses, one seen by the writer weighing 33½ lbs., whilst the largest piece of Prussian amber yet found weighs only 9·7 kilos. (21¼ lbs.).

Chemawinite (B. J. Harrington, 1891), Cedarite (R. Klebs, 1897), or Canadian amber, found as pale yellow fragments the size of a pea to that of a walnut on the beach of Cedar Lake, near Chemahawin in Saskatchewan.

Gedrite (O. Helm, 1878), a brittle, pale yellow resin found with Prussian amber, but differing from this in containing less oxygen and no succinic acid ; m.p. 140°.

Glessite (O. Helm, 1881), also found with Prussian amber ; it contains no succinic acid, but probably some formic acid ; m.p. 200°.

Roumanite, Romanite, Rumänite, or Roumanian amber (O. Helm, 1891), a brownish-yellow to brown resin, found in Tertiary sandstone at several places in Roumania ; it resembles Prussian amber in containing some succinic acid (0·3–3·2 p.c.), and is characterised by the relatively large amount of sulphur (1·15 p.c.) ; m.p. 300°.

Simetite, or Sicilian amber (O. Helm and H. Conwentz, 1886), a clear wine-red to garnet-red resin, remarkable for its beautiful green or blue fluorescence, found in the river Simeto and other parts of Sicily. It contains only 0·4 p.c. of succinic acid.

Stantienite (E. Pieszczek, 1880), a brown resin occurring with Prussian amber.

For several papers on amber and amber-like resins, by O. Helm and by P. Dahms, see Schr. natf. Ges. Danzig, vols. iv.–xii. (1878–1908). See also Max Bauer, Edelsteinkunde, 2nd edit. 1909, and English transl. (Precious Stones), by L. J. Spencer, 1904.   L. J. S.

AMBER, OIL OF. When amber is heated it softens, fuses, and gives off succinic acid, water, oil, and a combustible gas. If the residue (colophony of amber) be more strongly heated, a colourless oil passes over. These oils, according to Pelletier and Walter (Ann. Chem. Phys. [3] 9, 89), have the composition of oil of turpentine. By distilling with water, a pale-yellow oil, having a strong odour and acrid taste, can be obtained. It blackens and thickens on exposure to air and heat, boils at 86°, and has a sp.gr. of 0·758 at 24°. One part of the rectified oil mixed with 24 parts of alcohol (0·830) and 96 of ammonia, forms *eau de luce*, a celebrated old perfume. By mixing 'cau de luce' with nitric acid, artificial musk is made. Its solution in alcohol was formerly considered as a specific for whooping-cough (*v.* also OILS, ESSENTIAL, and RESINS).

AMBER VARNISH *v.* VARNISH.

AMBERGRIS. (*Ambregris*, Fr. ; *Ambra*, *Ambar*, Ger.) (J. Soc. Chem. Ind. 1890, 429.) Is found in the sea, near the coasts of tropical countries, and in the intestines of the spermaceti whale (*Physeter macrocephalus*).

Ambergris is generally found in fragments, but a piece has been obtained weighing 225 lbs. Its sp.gr. ranges from 0·780 to 0·926 (0·780 to 0·896 Brande, 0·908 to 0·920 Pereira). If of good quality, it adheres like wax to the edge of a knife with which it is scraped, retains the impression of the nails, and emits a fat odoriferous liquid on being penetrated with a hot needle. It is generally brittle, but on rubbing it with the nail it becomes smooth like hard soap. Its colour varies from black to white. Its smell is peculiar, and not easily counterfeited. It melts at 62·2°, at 100° it is volatilised as a white vapour ; on a red-hot coal it burns and is entirely dissipated. Water has no action on it ; acids, except nitric acid, act feebly upon it ; ether and the volatile oils dissolve it ; so do the fixed oils, and also ammonia when assisted by heat ; alcohol dissolves a portion of it.

The principal constituent of ambergris is *ambreïn (q.v.)* ; its inorganic constituents are carbonate and phosphate of calcium, with traces of ferric oxide and alkaline chlorides.

Used by perfumers. The Chinese test its purity by scraping it upon boiling tea, in which it should wholly melt.

AMBERITE *v.* EXPLOSIVES.

AMBLYGONITE. Fluo-phosphate of aluminium and lithium $AlPO_4,LiF$, crystallising in the anorthic system. It is usually found as whitish cleavage masses much resembling felspar in appearance, from which it is distinguished by its higher sp.gr. 3·01–3·09 and chemical characters. It occurs in granitic rocks at Montebras in France, Cáceres in Spain, Pala in California, &c. At each of the places named it has been mined for the preparation of lithium salts, the phosphate being a by-product. It contains about 10 p.c. of lithia.   L. J. S.

AMBREÏN. (*Ambreine*, Fr. ; *Ambarstoff*, Ger.) Isolated by Pelletier and Caventou, by digesting ambergris in hot alcohol, sp.gr. 0·827. It is of a brilliant white colour, has an agreeable odour, is destitute of taste, is insoluble in water, dissolves readily in alcohol and ether. Melts at 36°, and is volatilised above 100° ; is non-saponifiable ; is converted by nitric acid into *ambreic* acid. Ambreïn is probably impure cholesterol. Pelletier (Annalen, 6, 24) found it to contain C 83·3, H 13·3, and O 3·31 p.c.

AMBRITE. A brown translucent resin, similar to retinite, found in association with New Zealand coal.

AMENYL. Trade name for the *hydrochloride* of *methyl hydrastimide*. Forms yellowish needles, m.p. 227°. Soluble in hot water or alcohol.

AMERICAN COW or **MILK TREE WAX** *v.* WAX.

AMERICAN ELEMI *v.* OLEO-RESINS.

AMETHYST. A purple transparent variety of crystallised quartz (SiO_2), used as a gem-stone. So named, from ἀμέθυστος, 'not drunken,' owing to the ancient belief that the stone when worn as a charm prevented intoxication (*v.* QUARTZ). L. J. S.

AMETHYST. Tetramethyl safranine and tetraamyl safranine are found in commerce under this name (*v.* AZINES).

AMETHYST, ORIENTAL, *v.* CORUNDUM.

AMIANTHUS (*Amiante*, Fr.) *Mountain flax* (*v.* ASBESTOS).

AMIDASE *v.* ENZYMES.

AMIDE POWDER. An explosive similar to ordinary gunpowder, in which, in place of the sulphur, an ammonium salt is employed in combination with saltpetre, in such proportions that on ignition potassamide, volatile at high temperatures, is formed. This increases the useful effect of the explosive, which burns without residue (Gaens. Eng. Pat. 14412, 1885 ; J. Soc. Chem. Ind. 5, 678).

AMIDOAZOBENZENE or **ANILINE YELLOW** *v.* AZO- COLOURING MATTERS.

AMIDOGENE. An explosive made by dissolving 73 parts of potassium nitrate and 1 part magnesium sulphate in one-third their weight of boiling water ; 8 parts of ground wood charcoal, 8 parts of bran, and 10 parts of sulphur are added, and the whole is digested for two hours at 140° ; it is then dried at 50° and made into cartridges (Gemperle, J. Soc. Chem. Ind. 3, 191 ; 1, 201 ; Biedermann's Chem. Tech. Jahrb. 7, 146).

AMIDOGUANIDINE *v.* HYDRAZINES.

AMIDOL. Trade name for 2 : 4-diaminophenol hydrochloride, used as a photographic developer.

AMIDONAPHTHOLS *v.* AZO- COLOURING MATTERS.

AMIDONAPHTHOPHENAZINE *v.* AZINES.

AMIDOPHENOPHENANTHRAZINE *v.* AZINES.

AMINES. Amines or ' ammonia bases ' may be regarded as substances derived from ammonia by the substitution of hydrocarbon radicles for hydrogen. They may also be looked upon as derived from hydrocarbons by the replacement of one or more hydrogen atoms by NH_2 or its alkyl substitution products NHR or NRR'. The definition of the term would include alkyl derivatives of hydrazine and hydrazoic acid, and compounds such as nitrosamines, diazo- compounds ; and others which contain nitrogen linked to nitrogen or elements other than carbon, as well as to alkyl- residues. It also includes compounds in which the nitrogen forms part of a ring, as in pyridine, pyrrol, and their derivatives, among which the alkaloids may be mentioned. The majority of these more complex substances are treated of in detail in special articles (see arts. AZO- COLOURING MATTERS ; AZINES ; VEGETABLE ALKALOIDS ; BONE OIL ; QUINOLINE, &c.), and come within the scope of this only in so far as they possess the general characteristics of the ammonia bases.

Amines are classed as primary, secondary, or tertiary, according as one, two, or three of the hydrogen atoms of ammonia have been replaced by alkyl groups. Thus the general formula of the primary amines is NH_2R, of the secondary amines $NHRR'$, and of the tertiary amines $NRR'R''$, where R, R', and R'' may be identical or represent different alkyl groups. The reactions of the amines differ to some extent according as the substituting alkyl groups are (1) all aliphatic ; 2 mixed aliphatic and aromatic, with the nitrogen attached to the aliphatic residue, as in benzylamine ; (3) mixed aliphatic and aromatic, with the nitrogen attached to a carbon atom of the benzene ring, as in methyl aniline ; and (4) pure aromatic amines such as aniline itself, di- and tri-phenylamine, and their homologues. Substances of groups (1) and (2) will be referred to here as aliphatic and aromatic amines respectively, and those of groups (3) and (4) as aromatic amino- compounds. Aromatic amino- compounds serve as the starting materials in many of the different branches of the dyeing industry, and are prepared artificially in large quantities (*see* arts. ANILINE ; AZO- COLOURING MATTERS ; TRIPHENYLMETHANE COLOURING MATTERS ; DIPHENYLAMINE, &c.).

With the important exception of the vegetable alkaloids, the amines are not widely distributed in nature, though some of the lower members of the fatty series (methylamines) occur in plants and in the blood of some animals. They are, however, found as decomposition products of animal and vegetable organisms, and of mineral substances. Thus the methylamines are found in herring brine and in decomposing fish. Others, chiefly diamines, are found in certain pathological conditions of the urine, and as decomposition products of the animal tissues (ptomaïnes). The decomposition of proteins gives rise to large numbers of amino-acids. Aniline was first isolated as a product of the distillation of indigo, and it and its homologues as well as other bases are present in the distillates from bone oil (Dippel's oil), and of coal tar. A mixture of fatty amines is obtained in the dry distillation of the residues in the beet-sugar industry, and this, under the name of ' trimethylamine,' of which it contains about 5 p.c., is used in France for the preparation for industrial purposes of methyl chloride ; on account of the greater solubility of its hydrochloride, it has also been used instead of ammonia in the preparation of potassium carbonate, in a manner analogous to the Solvay method for the preparation of sodium carbonate, but the process does not seem to have been commercially successful.

General methods of preparation.

1. *By action of ammonia or its alkyl derivatives on substitution products (generally haloid or hydroxyl derivatives) of hydrocarbons.*

The method first described by Hofmann (Phil. Trans. 1850, 1, 93 ; 1851, 2, 357), of heating alkyl halides (preferably bromides or iodides) with ammonia, is available for the preparation of primary, secondary, and tertiary amines of the fatty series, and if aniline is substituted for ammonia, for the preparation of secondary, tertiary, and aromatic amino compounds. Quaternary ammonium compounds are also formed in the reactions, which may be represented as follows :—

$$NH_3 + RBr = NH_2R \cdot HBr.$$
$$NH_2R + R'Br = NHRR' \cdot HBr.$$
$$NHRR' + R''Br = NRR'R'' \cdot HBr.$$
$$NRR'R'' + R'''Br = NRR'R''R''' Br.$$
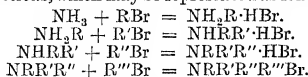
The reaction will take place, though only very slowly, in water solution, more quickly in alcoholic solution, and best on heating in alcoholic solution in sealed tubes at 100°. The products obtained may contain haloid salts of one or all of the possible amines, and of the quaternary bases.

In the preparation on the large scale of secondary and tertiary aromatic amino- compounds, *e.g.* dimethylaniline, the primary amine is heated under pressure directly with the alcohol and hydrochloric or sulphuric acid at 180°–200°. Here the alkyl group is exchanged directly for hydrogen without the intermediate separation of the alkyl halide. The presence of other negative groups in the benzene molecule increases the ease with which the NH_2 group can displace halogen groups. Thus the chlorine atoms of chlorbenzene can be replaced by NH_2 groups by the action of ammonia if the benzene ring also contains NO_2 groups.

Amines may also be obtained by heating zinc ammonium chloride with alcohols at 250°–260° (Merz and Gasiorowski, Ber. 1884, 17, 623).

Alcohols or phenols will react with ammonia or its alkyl derivatives on heating in the presence of zinc chloride, calcium chloride, or other catalytic agent (Merz and Weith, Ber. 1880, 13, 1298 ; Merz and Mueller, Ber. 1886, 19, 2901).

Mixtures of the vapours of alcohol and ammonia or primary amine led through tubes containing finely divided thoria or tungsten oxide at 360° give amines (Sabatier and Mailhe, Compt. rend. 1908, 148, 898).

Sodamide or its alkyl substitution products may be used instead of ammonia in the case of aliphatic amines.

$$NH_2Na + CH_3Cl = NH_2 \cdot CH_3 + NaCl$$

(Lebeau, Compt. rend. 1905, 140, 1042 ; Chablay, Compt. rend. 1905, 140, 1262). Sodamide will also react with anhydrous sulphuric esters of the aliphatic series, and with aromatic sulphonic acids to give primary amines (Jackson and Wing, Ber. 1886, 19, 902 ; Titherley, Chem. Soc. Trans. 1901, 79, 399).

2. *By reduction of nitrogen-containing substances.*

This method is chiefly important in the preparation of primary amines, and particularly in that of the aromatic amino- compounds, the nitro- compounds of which are easily obtained by direct nitration of the hydrocarbons, whereas the nitro- compounds of the aliphatic and aromatic amines are only obtained indirectly. Zinin in 1842 prepared aniline from nitrobenzene, by the action of alcoholic ammonium sulphide. On the commercial scale, as for instance in the preparation of aniline, iron and water with some hydrochloric acid is usually employed as the reducing agent. Nitro- compounds, however, as well as nitriles, oximes, and hydrazones, can be reduced to amines by electrolysis in dilute alcohol and sulphuric acid, using a nickel kathode (Pierron, Bull. Soc. chim. 1899, [3] 21, 780). A mixture of aliphatic aldehydes and ammonia is converted into amines if electrolysed in sulphuric acid solution with a lead kathode, the relative proportions of primary, secondary, and tertiary amines formed depending on the strength of the current, and the relative amounts of aldehyde and ammonia present (Knudsen, Ber. 1909, 42, 3994). Another method for the reduction of nitro compounds, nitriles, oximes, and hydrazones, consists in heating in a stream of hydrogen in the presence of finely divided nickel or copper (Sabatier and Senderens, Compt. rend. 1902, 125, 225). In all these methods the temperature must not be allowed to rise too high, or reduction of the amine to hydrocarbon and ammonia takes place. Other reducing agents employed are sodium amalgam and water, sodium and alcohol, sodium sulphide, zinc-dust and potash, stannous chloride, &c. Magnesium alkyl iodide (the Grignard reagent) sometimes acts as a reducing agent, and ethyl aniline has been obtained by treatment of nitrobenzene, with magnesium ethyl iodide (Oddo, Atti R. Accad. Lincei, 1904 (v.) 13, 2, 220).

Amides and amidines are also converted to amines by reduction with sodium and alcohol (Guerbet, Compt. rend. 1899, 129, 61).

$$R \cdot CONH_2 + 2H_2 = RCH \cdot NH_2 + H_2O.$$
$$RCNH \cdot NH_2 + 2H_2 = R \cdot CH_2 \cdot NH_2 + NH_3.$$
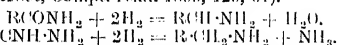
Condensation products of the action of primary amines and aldehydes of the type $R \cdot CH : N \cdot R'$, yield secondary amines on reduction.

$$R \cdot CH : NR' + H_2 = R \cdot CH_2 \cdot NHR'$$

(Stoermer and v. Lepel, Ber. 1896, 29, 2110 ; Brand, Ber. 1909, 42, 3460).
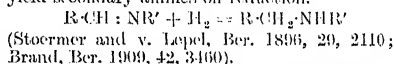
3. *From amides by the action of bromine and potash.* (Hofmann, Ber. 1882, 15, 762.)

This reaction is mainly applicable to the preparation of primary fatty amines, and gives good yields only with the lower members of the series. The first product of the reaction is a bromamide, and this on further treatment with potash gives amine, potassium bromide, and carbon dioxide, the alkyl group being transferred from the carbon to the nitrogen atom, as in the ' Beckmann rearrangement.'

$$CH_3 \cdot CONH_2 + KOH + Br_2$$
$$= CH_3 \cdot CONHBr + KBr + H_2O.$$
$$CH_3 \cdot CONHBr + KOH = CH_3 \cdot NH_2 + CO_2 + KBr.$$
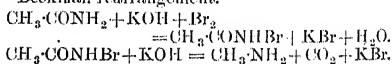
Azides on boiling with alcohol or water, and subsequent treatment with conc. HCl give amines.

$$R \cdot CO \cdot N_3 + C_2H_5 \cdot OH = RNH \cdot COOC_2H_5 + N_2.$$
$$R \cdot NH \cdot COOC_2H_5 + H_2O$$
$$= RNH_2 + CO_2 + C_2H_5OH$$
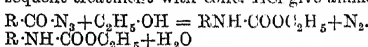
(Curtius, Ber. 1894 ; 27, 779, 1896, 29, 1166).

4. *By the action of alkalis on alkyl isocyanates.* (Wurtz, Annalen, 1849, 71, 330 ; 1850, 76, 317.)

The interest of this method is mainly historical, since it led to the discovery of the amines by Wurtz in 1848. Primary amines are the chief product, but secondary and tertiary amines are also formed in small quantities.

$$C_2H_5NCO + H_2O = C_2H_5 \cdot NH_2 + CO_2.$$
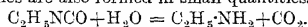
5. *By hydrolysis of alkyl esters of thio-carbamines and isocyanides with concentrated acids.*

$$C_2H_5NCS + H_2O = C_2H_5 \cdot NH_2 + COS.$$
$$C_2H_5NC + H_2O = C_2H_5 \cdot NH_2 + HCOOH.$$
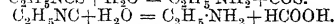
6. *From compounds which certain substances form with alkyl iodides.*

(*a*) Hexamethylene tetramine, formed by the action of ammonia on formaldehyde, gives addition compounds of the type $C_6H_{12}N_4 \cdot RI$ with alkyl iodides. These on treatment with HCl and alcohol are decomposed, giving primary amines (Delépine, Compt. rend. 1897, 124, 292; Ann. Chim. Phys. 1898, [7] 15, 508).

(*b*) Phthalimide, on treatment with alcoholic potash, gives potassium phthalimide, and this gives an alkyl derivative on treatment with alkyl iodide, which on hydrolysis with fuming HCl yields a primary amine.

$$C_6H_4(CO)_2NK + RI = C_6H_4(CO)_2NR + KI.$$
$$C_6H_4(CO)_2NR + 2H_2O = C_6H_4(COOH)_2 + NH_2R$$

(Gabriel, Ber. 1887, 20, 2224; 1891, 24, 3104).
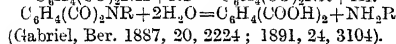
(*c*) Magnesium alkyl iodides form addition compounds with phenyl *iso*cyanate; these, on treatment with water are converted into anilides, which yield amines on saponification (Blaise, Compt. rend. 1901, 132, 38, 478, 978).

(*d*) Sodium acetamide, if treated with alkyl iodide, gives mono- and di-alkyl derivatives of formula $R \cdot CONHR$, and $R \cdot CONRR'$, and these on saponification yield primary and secondary

amines respectively (Titherley, Chem. Soc. Trans. 1901, 79, 399).

7. *By distillation of amino-acids with baryta.*

$$CH_2CH{<}^{COOH}_{NH_2} = CH_2 \cdot CH_2 \cdot NH_2 + CO_2.$$
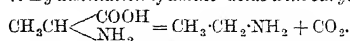
8. *Aliphatic primary and secondary amines may be obtained by the action of potash on the p-nitroso derivatives of secondary and tertiary aromatic amino-compounds.*

$$NO \cdot N \cdot C_6H_4(CH_3)_2 + KOH$$
$$= C_6H_4 \cdot NO \cdot OK + N(CH_3)_2H.$$
$$NO \cdot C_6H_4 \cdot NHCH_3 + KOH$$
$$= C_6H_4 \cdot NO \cdot OK + NH_2 \cdot CH_3.$$
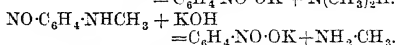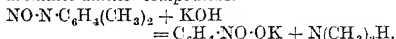
9. *Tertiary amines can be obtained by heating primary and secondary bases with excess of potassium alkyl sulphate.*

$$RR'NH + CH_3OSO_3K = RR'NCH_3 + HOSO_3K.$$
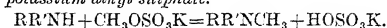
General Properties.

The amines of the aliphatic series are volatile inflammable substances, the lower members being gases or liquids with low boiling-points, very soluble in water and strongly alkaline to litmus; the density of the liquid members of the series is about 0·75 that of water, and increases slightly with increase in the molecular weight. Their basicity, measured by the conductivity method, is considerably greater than that of ammonia, and they will saponify esters and precipitate oxides from the salts of many of the heavy metals. They have an ammoniacal and fishy odour. The smell, inflammability, boiling-point, and solubility in water become less with increase in the molecular weight, and the highest known members are odourless solids at ordinary temperatures. They react with moist air with formation of

ALIPHATIC AMINES.

Alkyl groups	Primary compounds			Secondary compounds		Tertiary compounds	
	M.pt.	B.pt.	Sp.gr.	B.pt.	Sp.gr.	B.pt.	Sp.gr.
Methyl	—	−6·7°	0·699 (−11°)	+7°	0·686 (−6°)	+3·5°	0·662 (−5°)
Ethyl	−83·8°	+19°	0·708 (−2°)	56°	0·711 (+15°)	90°	0·735 (+15°)
Propyl	—	49°	0·728 (0°)	110°	0·738 (20°)	156°	0·771 (0°)
iso-Propyl	—	32°	0·690 (18°)	84°	0·724 (15°)	—	—
prim. n-Butyl	—	77·8°	0·742 (15°)	160°	—	216·5°	0·791 (0°)
iso-Butyl	—	66°	0·735 (15°)	136°	—	187°	0·785 (21°)
sec. Butyl	—	63°	0·718 (20°)	—	—	—	—
tert. Butyl	—	43·8°	0·698 (15°)	—	—	—	—
prim. n-Amyl	—	104°	0·766 (19°)	—	—	—	—
iso-Amyl	—	95°	0·750 (18°)	187°	0·782 (0°)	235°	—
tert. Butyl-methyl	—	82°–83°	—	—	—	—	—
sec. n-Amyl	—	90°–91°	0·749 (20°)	—	—	—	—
sec. iso-Amyl	—	83°–84°	0·757 (18·5°)	—	—	—	—
tert. Amyl	—	78·5°	0·748 (15°)	—	—	—	—
prim. n-Hexyl	—	129°	—	—	—	260°	—
,, ,, Heptyl	—	153°	0·777 (20°)	—	—	—	—
,, ,, Octyl	—	175°–177°	0·777 (26·8°)	297°	—	366°	—
,, ,, Nonyl	—	190°–192°	—	—	—	—	—
,, ,, Decyl	+17	216°–218°	—	—	—	—	—
,, ,, Undecyl	15°	232°	—	—	—	—	—
,, ,, Duodecyl	27°	248°	—	—	—	—	—
,, ,, Tridecyl	27°	265°	—	—	—	—	—
,, ,, Tetradecyl	37°	162°(15 mm.)	—	—	—	—	—
,, ,, Pentadecyl	36·5°	298°–301°	—	—	—	—	—
,, ,, Hexadecyl	45°	187°(15 mm.)	—	—	—	—	—
,, ,, Heptadecyl	49°	335°–340°	—	—	—	—	—

HOMOLOGUES OF ANILINE.

Primary aromatic amino- compounds

Formula	Popular name	Systematic name	M.pt.	B.pt.	Sp. gr.	M. pt. of mon-acetyl deriv.
$C_6H_5\cdot NH_2$	aniline	aminobenzene	$-8°$	$183°$	$1·024\,(16°)$	$115°$
$CH_3\cdot C_6H_4\cdot NH_2$	ortho toluidine	1-methyl-2-aminobenzene	—	$199°$	$0·999\,(20°)$	
						$110°$
	meta ,	1-methyl-3-aminobenzene	—	$199°$	$0·998\,(25°)$	
						$65·5°$
	para ,	1-methyl-4-aminobenzene	$+42·8°$	$198°$	—	$153°$
$(CH_3)_2C_6H_3\cdot NH_2$	1-2-3 ortho xylidine	1:2-dimethyl-3-aminobenzene	—	$223°$	$0·991\,(15°)$	$134°$
	1-2-4 ,, ,,	1:2-dimethyl-4-aminobenzene	$+49°$	$226°$	$1·076\,(17°)$	$90°$
	1-3-2 meta ,,	1:3-dimethyl-2-aminobenzene	—	$215°$	—	$176·5°$
	asymm. meta xylidine	1:3-dimethyl-4-aminobenzene	—	$215°$	$0·918\,(25°)$	$129°$
	symm. meta xylidine	1:3-dimethyl-5-aminobenzene	—	$223°$	$0·972\,(15°)$	$140·5°$
	para xylidine	1:4-dimethyl-2-aminobenzene	$+15·5°$	$215°$	$0·980\,(15°)$	$139·5°$
$C_2H_5\cdot C_6H_4\cdot NH_2$	para amino ethyl benzene	1-ethyl-4-amino-benzene	$-5°$	$214°$	$0·975\,(22°)$	$94·5°$
$(CH_3)_3C_6H_2\cdot NH_2$	mesidine	1:3:5-trimethyl-2-aminobenzene	—	$233°$	—	$216°$
	pseudo-cumidine	1:2:4-trimethyl-5-aminobenzene	$+68°$	$234°$	—	$164°$
$(C_2H_5\cdot CH_2)C_6H_4\cdot NH_2$	para amino propyl benzene	1-propyl-4-aminobenzene	—	$225°$	—	—
$(CH_3)_2CH\cdot C_6H_4\cdot NH_2$	cumidine	1-isopropyl-4-aminobenzene	—	$218°$	—	$102·5°$
$(CH_3)_4C_6H\cdot NH_2$	prehnidine	1:2:3:4-tetramethyl-5-aminobenzene	$+70°$	$260°$	—	$172°$
	isoduridine	1:2:3:5-tetramethyl-4-aminobenzene	$+24°$	$255°$	$0·978\,(24°)$	$215°$
$(CH_3)(C_3H_7)C_6H_3\cdot NH_2$	carvacrylamine	1-methyl-4-isopropyl-2-aminobenzene	—	$241°$	$0·944\,(24°)$	$72°$
	thymylamine	1-methyl-4-isopropyl-3-aminobenzene	—	$230°$	—	$112·5°$
$(CH_3)_2CH\cdot CH_2\cdot C_6H_4\cdot NH_2$	para amino isobutyl benzene	1-isobutyl-4-aminobenzene	$+17°$	$230°$	$0·937\,(25°)$	$170°$
$(CH_3)_5C_6\cdot NH_2$	amino pentamethyl benzene	pentamethyl amino-benzene	$152°$	$278°$	—	$213°$
$C_5H_{11}\cdot C_6H_4\cdot NH_2$	amino isoamyl benzene		—	$260°$	—	—
$C_8H_{17}\cdot C_6H_4\cdot NH_2$	para amino octyl benzene	1-octyl-4-aminobenzene	$+19·5°$	$310°$	—	$93°$
$C_{16}H_{33}\cdot C_6H_4\cdot NH_2$	amino cetyl benzene	hexadecyl aminobenzene	$53°$	$255°\,(14\,mm.)$	—	$104°$
$C_{18}H_{37}\cdot C_6H_4NH_2$	amino octadecyl benzene	octadecyl aminobenzene	$61°$	$274°\,(15\,mm.)$	—	

carbonates. Aromatic amines (benzylamine and its homologues) closely resemble the aliphatic amines, but are not quite so strongly basic in character, owing to the presence of the negative phenyl group. The aromatic amino- compounds (aniline and its homologues) are less basic than ammonia, and the basicity diminishes with increase of the number of phenyl- groups attached to the nitrogen atom. Thus the salts of diphenylamine are hydrolysed by water to a greater extent than those of aniline, whilst triphenylamine is a neutral body and forms no salts with acids. Comparatively few amines are known which contain only aromatic groups ; of these aniline and diphenylamine are prepared on the large scale in the dyeing industry, as well as many secondary and tertiary amino compounds containing both fatty and aromatic groups.

The above lists of the chief homologues of methylamine and aniline (*see* pp. 129, 130) are taken from Meyer and Jacobsen's Lehrbuch der Organischen Chemie.

All classes of amines form addition products with acids, containing one molecule of base to one molecule of monobasic acid. Compounds containing three molecules of HCl to one of amine have also been obtained (Korczynski, Ber. 1908, 41, 4379). The picrates are specially characteristic, and are used for the identification of the amines, as are also the double salts with platinum and gold chlorides, which have the general formulæ $B_2H_2PtCl_6$ and $BHAuCl_4$ respectively. Many aliphatic amines form hydrates with one molecule of water of crystallisation. Double salts with mercuric chloride and stannic chloride, and with silver salts, crystallise well, and organic analogues of ammonium pyrophosphate and arsenate are known, but are not very stable (Brisac, Bull. Soc. chim. 1903, [3] 29, 591). With alkyl halides they form quaternary ammonium compounds of the type NRR′R″R‴I, where RR′R″R‴ may be the same or different radicles. · In cases where these radicles are all different, the substances are capable of existing in two enantiomorphous optically active

forms, and a number of these have been isolated. The quaternary ammonium compounds, unlike their inorganic analogues, are not decomposed on boiling with potash; on heating alone they give tertiary amines and alkyl halides. The corresponding bases are obtained from their halides by treatment with moist silver oxide; they are strongly alkaline to litmus, and the solutions generally decompose easily on evaporation, but some of the aliphatic members have been obtained crystalline by evaporation *in vacuô*.

The formation of quaternary ammonium compounds by addition of excess of methyl iodide to an amine gives a quantitative method for the determination of the number of replaceable hydrogen atoms in the substance. Analysis of the original compound and of its quaternary methyl derivative gives the number of methyl groups which have entered into the molecule.

The chemical behaviour of many substances varies with the different classes of amines, and separation and purification of the amines formed in many of the methods above referred to may be carried out by making use of such differences. Primary and secondary amines usually give similar reactions, whilst tertiary amines are more stable, in accordance with the general rule for compounds which contain carbon atoms linked to the maximum possible number of hydrogen atoms.

Reactions.

1. *With nitrous acid.*

Primary amines, on boiling with potassium or sodium nitrite in acid solution, give alcohols or phenols with evolution of nitrogen.

$$RNH_2 + HONO = ROH + N_2 + H_2O.$$
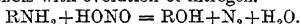
Secondary amines give nitrosamines, which on boiling with conc. HCl are again transformed into the original amines.

$$RR'NH + HONO = RR'N \cdot NO + H_2O.$$
$$RR'N \cdot NO + 2HCl = RR'NH \cdot HCl + NOCl.$$
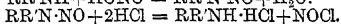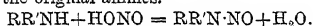
Tertiary amines do not react.

Primary aromatic amino compounds react differently if their solutions are kept cooled. They give diazo- compounds according to the following equation:—

$$RNH_2, HCl + HONO = RN : NCl + 2H_2O.$$
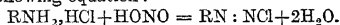
This reaction is of the greatest importance, for the diazo- compounds are very unstable, and on treatment with various substances either form substitution products of benzene hydrocarbons with evolution of nitrogen, or retain the nitrogen and form azo- compounds, which are the parent substances of the azo- dyes. Thus, if the diazo- compound be boiled with water, alcohol, cuprous chloride, bromide, or cyanide, phenol, benzene, chlor, brom, or cyan, derivatives respectively are produced. If the diazo- compound is treated with a substance containing a phenol or aromatic amino- group, a coloured substance is formed which is capable of fixing itself as a dye on a fabric. Compounds derived from unsubstituted amines have only a limited application for dyeing purposes, as they are generally insoluble in water; the sulphonic acids derived from them are, however, generally soluble, and are used extensively (*see* art. AZO-COLOURING MATTERS). The reactions are expressed by the following equations:—

$$C_6H_5N_2Cl + C_6H_5OH = C_6H_5N : NC_6H_4OH + HCl$$
$$C_6H_5N_2Cl + C_6H_5N(CH_3)_2$$
$$= C_6H_5N : NC_6H_4N(CH_3)_2 + HCl$$
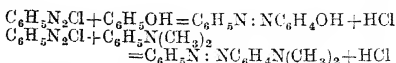
Tertiary aromatic compounds, such as dimethyl aniline, react with nitrous acid to form *p*-nitroso compounds, where the nitroso nitrogen is attached to the carbon of the benzene ring in the para-position to the substituted amino-group. These are highly coloured substances, and serve as intermediate compounds in the production of certain colouring matters (methylene blue, &c.), which are used in the colour industry. On treatment with caustic potash they give secondary amines and salts of nitroso phenol.

2. *With chlorides of aromatic sulphonic acids.*

Primary and secondary amines in strong alkaline solution are converted into amides by shaking with chlorides of aromatic sulphonic acids; of these amides, $Ph \cdot SO_2NHR$ and $PhSO_2NRR'$ respectively, the first only are soluble in dilute alkalis with formation of salts. Tertiary amines do not react. The primary and secondary amines can be regenerated from the amides by boiling with conc. HCl or H_2SO_4 at 120°–150° (Hinsberg, Ber. 23, 2963; Annalen, 1891, 265, 178).

3. *With acetyl chloride or acetic anhydride.*

Primary and secondary amines give, as a rule, acetyl derivatives which are insoluble in cold water; tertiary amines either do not react, or form soluble acetates and hydrochlorides. The primary and secondary amines may be regenerated by saponification of the acetyl derivatives. Since the velocity of the formation of the acetyl derivative of the primary is much greater than that of the secondary amine, a method based on this difference in property has been used to separate the two (Menschutkin, Chem. Zentr. 1900, 1, 1071; Potozki and Gwosdow, *ibid.* 1903, ii. 339).

The action of benzoyl chloride is similar to that of acetyl chloride.

4. *With oxalic esters.*

Several of the aliphatic primary and secondary amines react with ethyl oxalate, the former giving solid diamides and the latter liquid oxamic esters. Tertiary amines do not react. Primary and secondary amines are regenerated by boiling with potash (Hofmann, Ber. 1870, 3, 109, 776; Duvillier and Buisine, Ann. Chim. Phys. [5] 23, 299).

5. *With magnesium methyl iodides.*

Primary amines react, giving two molecules of methane for every molecule of amine:

$$RNH_2 + 2MeMgI = RN(MgI)_2 + 2CH_4.$$
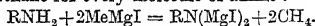
Secondary amines react in a similar manner, but give one molecule of methane for every molecule of amine:

$$RR'NH + CH_3MgI = RR'NMgI + CH_4.$$
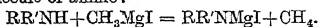
Tertiary amines either do not react or they form addition compounds with the reagent (Sudborough and Hibbert, Chem. Soc. Trans. 1909, 95, 477).

6. *With o-xylylene bromide.*

Primary amines react, giving two molecules of HBr and liquid derivatives of *o*-xylyleneimine (dihydro*iso*indol).

Secondary amines react, giving crystalline quaternary ammonium bromides and one molecule of HBr:

$$C_6H_4{<}^{CH_2Br}_{CH_2Br} + NH_2R$$

$$= C_6H_4{<}^{CH_2}_{CH_2}{>}NR + 2HBr.$$

$$C_6H_4{<}^{CH_2Br}_{CH_2Br} + NHRR'$$

$$= C_6H_4{<}^{CH_2}_{CH_2}{>}N{<}^R_{R'} + HBr.$$
$$\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\;\,Br$$
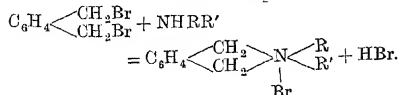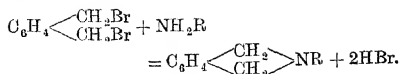
Tertiary aliphatic amines give addition products of one molecule of xylylenebromide with two of amine. Tertiary aromatic amines and amino- compounds do not react (Scholtz, Ber. 1898, 31, 1707).

7. *With aromatic aldehydes.*

Primary and secondary amines form compounds with loss of water :

$$C_6H_5CHO + NH_2R = C_6H_5CHNR + H_2O.$$
$$C_6H_5CHO + 2NRR'H = C_6H_5CH(NRR')_2 + H_2O.$$
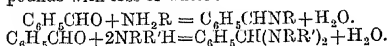
Tertiary amines do not react (Schiff, Annalen, 159, 159).

8. *With chloroform and potash.*

Primary amines give *iso*cyanides on warming.

$$RNH_2 + CHCl_3 + 3KOH = RNC + 3KCl + 3H_2O$$

(Hofmann, Ber. 3, 767).
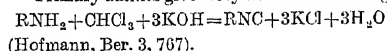
Secondary and tertiary amines give no characteristic reaction.

9. *With carbon disulphide.*

Aliphatic primary and secondary amines react as follows :—

$$CS_2 + 2NH_2R = SC{<}^{NHR}_{SH.NH_2R.}$$

$$CS_2 + 2NHRR' = SC{<}^{NRR'}_{SH.NHRR'.}$$
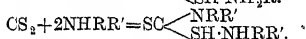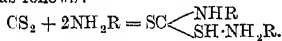
On boiling the product of the action of CS_2 on primary amines with metallic salts ($HgCl_2$ or $FeCl_3$), mustard oils are produced, and primary amines partly regenerated.

$$SC{<}^{NHR}_{SH.NH_2R} = SCNR + H_2S + NH_2R.$$

(Hofmann, Ber. 8, 105, 461; 14, 2754; 15, 1290).
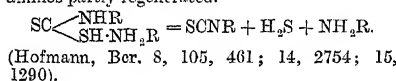
Aromatic amines give substituted thioureas.

$$2RNH_2 + CS_2 = H_2S + (RNH)_2CS.$$
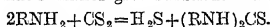
10. *With the alkali metals.*

Primary and secondary amines dissolve with evolution of hydrogen and formation of substances of the type $RNHK$ or RNK_2. Tertiary amines do not react.

11. *With oxidising agents.*

Oxidation with potassium permanganate decomposes aliphatic amines with formation of aldehydes and acids.

With Caro's acid (H_2SO_5), primary amines of the type RCH_2NH_2 are oxidised to hydroxylamines and hydroxamic acids, all of which give a characteristic colouration with ferric chloride. Ketoximes are formed from amines of the type $RR'CH\cdot NH_2$, whilst those of the type $RR'R''C\cdot NH_2$ give nitroso- and nitro- derivatives (Bamberger, Ber. 1902, 35, 4293 ; 1903, 36, 710).

With hydrogen peroxide aliphatic, secondary, and tertiary amines give hydroxylamines and N-oxides of type $RR'NOH$ and $RR'R''NO$ (Dunstan and Goulding, Chem. Soc. Trans. 75, 1104).

Oxidation of aniline and its para compounds gives quinone.

DIAMINES.

These may be regarded as derived from hydrocarbons by replacement of two hydrogen atoms by two amino- groups, or from two molecules of ammonia by replacement of two hydrogen atoms one from each molecule by a hydrocarbon residue. Certain of them occur as decomposition products of the animal organism, the chief of these being *putrescine* (tetramethylene diamine), and *cadaverine* (pentamethylene diamine). Diamino- acids are an important product of the decomposition of proteins.

Preparation.—The methods are entirely analogous to those used in the preparation of monamines. Aliphatic diamines are obtained by the action of aqueous ammonia on dihalogen derivatives of hydrocarbons ; this method is not generally applicable to the preparation of aromatic mono- or diamino- compounds, but a modification of it, which consists in treatment of *p*-chlormonamines with aqueous ammonia in presence of copper salts, is used in the commercial manufacture of *p*-phenylene diamine and its homologues (Ger. Pat. 204848, 1908). Aromatic diamino- compounds are prepared on the commercial scale chiefly by the reduction of dinitro- compounds ; but practically all the methods for the production of monamines are also available for that of diamines.

Properties. — The aliphatic diamines are strongly basic substances, their basicity increasing with the number of methylene groups (Bredig, Zeitsch. physical. Chem. 1894, 13, 308). Their boiling-points are much higher than those of the corresponding monamines. Their hydroxides, which are diacid bases, are extremely stable, and are only decomposed on boiling with caustic alkalis or distillation over metallic sodium. The list of the chief aliphatic diamines and their physical constants (*see* p. 133) is taken from Meyer and Jacobson's Lehrbuch der Organischer Chemie. The lower members of the aromatic diamino compound differ from the corresponding monamines by being easily soluble in water. Their solutions in water are easily oxidised, but the dry bases are stable in air.

Reactions.—Diamines give the ordinary reactions characteristic of the amino- group, but primary aromatic o-amino- compounds and to some extent aliphatic diamines, possess in addition, the property of forming condensation products containing nitrogen rings. *m-* and *p-* diamines do not exhibit this property.

1. *With aldehydes.*

With aliphatic diamines, cyclic compounds are formed as well as the ordinary alkylidene bases. Thus the action of formaldehyde on cold solutions of ethylene diamine results in the formation of a compound $C_8H_{16}N_4$, to which the formula

$$CH_2{-}N{-}CH_2{-}N{-}CH_2$$

$$\diagdown CH_2 \, CH_2 \diagup$$

$$CH_2{-}N{-}CH_2{-}N{-}CH_2$$
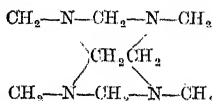
has been assigned (Bischoff, Ber. 1898, 31, 3254).

Aromatic o-diamino- compounds give aldehydines or anhydro bases :

ALIPHATIC DIAMINES.

	Formula	M.pt.	B.pt.	Sp.gr.
Ethylenediamine .	$NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$	$+8 \cdot 5^\circ$	$116 \cdot 5^\circ$	$0 \cdot 902$ (15°)
Propylene ,, .	$CH_3 \cdot CH(NH_2)CH_2 \cdot NH_2$		$119^\circ-120^\circ$	$0 \cdot 878$ (15°)
Trimethylenediamine	$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$		$135^\circ-136^\circ$	
			$(788$ mm.$)$	
$\alpha\beta$-diaminobutane .	$CH_3 \cdot CH_2 \cdot CH(NH_2) \cdot CH_2 \cdot NH_2$		$130^\circ-155^\circ$	
$\alpha\gamma$- ,, ,, .	$CH_3 \cdot CH \cdot (NH_2) \cdot CH_2 \cdot CH_2 \cdot NH_2$		141°	
			$(788$ mm.$)$	
$\alpha\delta$- ,, ,, .	$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$	$27^\circ-28^\circ$	$158^\circ-160^\circ$	
$\beta\gamma$- ,, ,, .	$CH_3 \cdot CH(NH_2)CH(NH_2)CH_3$	only known	as its salts	
$\alpha\epsilon$- ,, pentane .	$NH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$		$178^\circ-179^\circ$	$0 \cdot 917$ (0°)
	$CH_3CH(NH_2)CH_2 \cdot CH(NH_2)CH_3$	α modifica-	$46^\circ-47^\circ$	
		tion	$(20$ mm.$)$	
		β modifica-	$43^\circ-44^\circ$	
β-methyl-$\alpha\delta$-diaminobutane .	$NH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot NH_2$	tion	$(11-12$ mm.$)$	$0 \cdot 8836 \left(\frac{20^\circ}{4^\circ}\right)$
		inactive	$172^\circ-173^\circ$	
		form		
$\alpha\zeta$-diaminohexane . .	$NH_2 \cdot CH_2(CH_2)_4CH_2 \cdot NH_2$	active form	170°	
		$39^\circ-40^\circ$	100°	
$\beta\epsilon$- ,, ,, . .	$CH_3 \cdot CH(NH_2)(CH_2)_2CH(NH_2)CH_3$		$(20$ mm.$)$	
		ϕ derivative	$175 \cdot 5^\circ$	
			$(753$ mm.$)$	
			$174 \cdot 5^\circ-175 \cdot 5^\circ$	
			$(752$ mm.$)$	
β-methyl-$\alpha\delta$-diaminopentane .	$NH_2 \cdot CH_2 \cdot CH(CH_2) \cdot CH \cdot CH \cdot NH \cdot CH_3$		175°	
β-methyl-$\alpha\epsilon$- ,, ,,	$NH_2 \cdot CH_2 \cdot CH \cdot CH_3)CH_2 \cdot CH_2 \cdot NH_2$		$78^\circ-80^\circ$	
			$(13$ mm.$)$	
$\beta\gamma$-dimethyl-$\beta\gamma$-diaminobutane	$(CH_3)_2C(NH_2) \cdot C(NH_2)(CH_3)_2$	$97^\circ-99^\circ$	$147^\circ-149^\circ$	
			$(740$ mm.$)$	
$\alpha\eta$-diaminoheptane . . .	$NH_2(CH_2)_7NH_2$	$28^\circ-29^\circ$	$223^\circ-225^\circ$	
$\alpha\theta$-diaminooctane . .	$NH_2(CH_2)_8NH_2$	52°	$225^\circ-226^\circ$	
$\beta\epsilon$-dimethyl-$\beta\epsilon$-diaminohexane .	$(CH_3)_2C(NH_2)(CH_2)_2(NH_2)C(CH_3)_2$	solidifies	186°	$0 \cdot 858 \left(\frac{0^\circ}{0^\circ}\right)$
		at 0°	$(758$ mm.$)$	
$\gamma\delta$-dimethyl-$\gamma\delta$-diaminohexane	$C_2H_5 \cdot C(CH_3)NH \cdot NH \cdot C \cdot CH_3 \cdot C_2H_5$	only known	as its salts	—
$\alpha\iota$-diaminononane . .	$NH_2(CH_2)_9NH_2$	$37^\circ-37 \cdot 5^\circ$	$258^\circ-250^\circ$	—
$\beta\zeta$-dimethyl-$\beta\zeta$-diaminoheptane	$(CH_3)_2C(NH_2)(CH_2)_3(NH_2)C(CH_3)_2$		$204^\circ-206^\circ$	$0 \cdot 8554 \left(\frac{0^\circ}{0^\circ}\right)$
			$(749$ mm.$)$	
$\alpha\kappa$-diaminodecane . .	$NH_2(CH_2)_{10}NH_2$	$61 \cdot 5^\circ$	140°	
			$(12$ mm.$)$	
$\beta\eta$-dimethyl-$\beta\eta$-diaminooctane	$(CH_3)_2C(NH_2)(CH_2)_4(NH_2)C(CH_3)_2$	31°	$226^\circ-229^\circ$	$0 \cdot 8344 \left(\frac{28^\circ}{0^\circ}\right)$
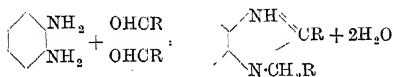
(Ladenburg and Engelbrecht, Ber. 1878, 11, 1653; Hinsberg, ibid. 1886, 19, 2025).

The aldehydines are strongly basic bodies, and not decomposed on boiling with dilute acids and alkalis. They are very stable towards oxidising and reducing agents. Their derivatives are used as dyes.

p- and m-diamines give alkylidene bases.

2. With 1.2-dicarbonyl compounds (aldehydes or ketones).

o-Diamino compounds react to give quinoxaline (azine) derivatives (Hinsberg, Annalen, 342, 1886);
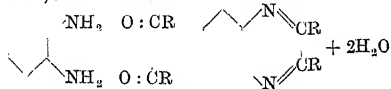
3. With nitrous acid.

o-Diamino- compounds form azimines (Ladenburg)
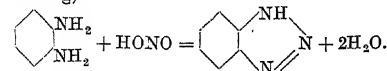
Diamino- compounds both m- and p- will react in the ordinary way in presence of much hydrochloric acid, giving bis-diazo- compounds;

in neutral solutions m-diamino- compounds give triamino azo benzene and its homologues. The reaction in the case of m-phenylene diamine is :

$$2C_6H_4(NH_2)_2 + HONO$$
$$= NH_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_3(NH_2)_2.$$
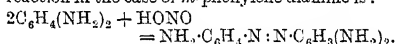
The substances formed are brown and very deeply coloured. The reaction is used as a test for the presence of nitrites in water analysis (Griess, Ber. 1878, 11, 624).

Aliphatic diamines give glycols and oxides.

4. With organic acids, acid chlorides or anhydrides.

Aliphatic diamines and m- and p-diaminocompounds form normal derivatives; in the cases of aliphatic substances, these derivatives are partially decomposed on heating, giving cyclic compounds of the iminoazole type:
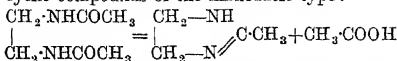
o-Diamino- compounds give similar compounds, without the intermediate formation of the acyl derivative :
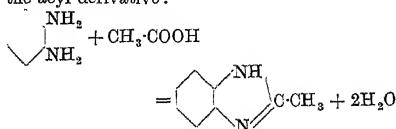
5. With mineral acids.
All diamines form stable salts. Those of

the aliphatic series are decomposed on heating with separation of ammonium salt and formation of cyclic compounds. Thus, tetramethylene diamine gives pyrrolidine and pentamethylene diamine gives piperidine:

$NH_2(CH_2)_4NH_2,HCl = NH_4Cl + H_2C$⟨—$CH_2$

$$H_2C\quad CH_2$$
$$NH$$

$$CH_2$$
$NH_2(CH_2)_5NH_2,HCl = NH_4Cl + H_2C$⟨$\quad$ CH_2
$$H_2C\quad CH_2$$
$$NH$$
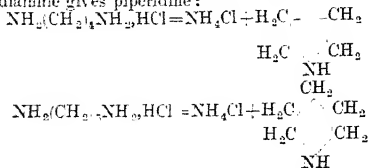
The higher homologues, however, do not form ring compounds containing a corresponding number of atoms in the ring. Thus, octomethylene diamine hydrochloride, on heating, does not give octomethylene imine, which would contain a ring of nine atoms, but 2-butylpyrrolidine. Similarly, decamethylene diamine gives 2-hexylpyrrolidine (Blaise and Houillon, Compt. rend. 1906, 142, 1541; 1906, 143, 361).

The aromatic diamines are the starting-points for the preparation of a large number of dyes, and in some are of commercial importance. The following are the chief members of the series:—

o-Phenylenediamine $C_6H_4(NH_2)_2$. First obtained by various by the distillation of o-m- and m-p- diaminobenzoic acid:

$$C_6H_3.COOH.NH_2 = C_6H_4(NH_2)_2 + CO_2$$
$$(1, 2, 3, or 1, 3, 4)\qquad\qquad (1, 2)$$
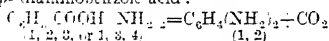
(J. pr. Chem. [2] 3, 143). By the reduction of o-nitraniline $C_2H_4(NO_2)(NH_2)$ (1, 2) (Zincke and Sintenis, Ber. 6, 123), or of o-dinitrobenzene $C_6H_4(NO_2)_2$ (1, 2) (Rinne and Zincke, Ber. 7, 1374), with tin and hydrochloric acid.— Crystallises from water in laminæ, melting at 102°. Boils at 252°. Readily soluble in water, alcohol. and ether. Diacid base, the sulphate $2(C_6H_4(NH_2)_2,H_2SO_4)3H_2O$ forms nacreous laminæ. It gives all the reactions for o-diaminocompounds referred to above. On oxidation with ferric chloride it gives a red compound, diaminophenazine:

$$NH_2$$
$$C_6H_4(NH_2)_2 + 3O$$
$$NH_2$$

$$C_6H_3(NH_2)_2 + 3H_2O$$
$$N$$
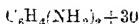
m-Phenylenediamine $C_6H_4(NH_2)_2$. By reducing m-dinitrobenzene or m-nitraniline with iron filings and acetic acid (Hofmann, Proc. Roy. Soc. 11, 518; 12, 639), or with tin and hydrochloric acid (Gerdemann, Zeitsch. f. Chem. 1865, 61). By reducing either (1. 2, 4)- or (1, 2, 6)-dinitrobenzoic acid with tin and hydrochloric acid, the carboxyl group being eliminated in the process (Zincke and Sintenis, Ber. 5, 791; Griess, Ber. 7, 1223). On a manufacturing scale it is prepared by reducing dinitrobenzene with iron turnings and hydrochloric acid.—Separates from its solutions as an oil which does not readily solidify unless brought in contact with a crystal of the base. Melts at 63°, and boils at 287°. Readily soluble in

water. It gives the typical reactions of m-diamino- compounds (see above).

By the action of a diazobenzene salt on m-phenylenediamine, chrysoïdine (unsymmetrical diaminoazobenzene) is produced:

$$C_6H_5N_2Cl + C_6H_4(NH_2)_2$$
$$= HCl + C_6H_5N : N \cdot C_6H_3(NH_2)_2.$$
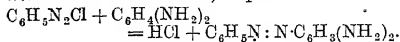
In the manufacture of phenylene-brown and chrysoïdine the solution of crude m-phenylenediamine hydrochloride obtained by the reduction of m-dinitrobenzene is employed, without first isolating the base. A violet colouring matter is obtained by heating m-phenylenediamine with aniline hydrochloride to 190°–200°, and a blue colouring matter by heating it with m-phenylenediamine hydrochloride (Krause, Ber. 9, 835).

p-Phenylenediamine $C_6H_4(NH_2)_2$. Obtained by reducing p-dinitrobenzene (Rinne and Zincke, Ber. 7, 871), or p-nitraniline (Hofmann, Proc. Roy. Soc. 12, 639), or aminoazobenzene (Martius and Griess, J. pr. Chem. 97, 263), with tin and hydrochloric acid, aniline being formed simultaneously in the case of aminoazobenzene. Along with diamirodiphenylamine by reducing aniline-black with tin and hydrochloric acid or with hydriodic acid and amorphous phosphorus (Nietzki, Ber. 11, 1097). By distilling (1, 2, 5)-diaminobenzoic acid (Griess, Ber. 5, 200). By action of p-chloraniline on aqueous ammonia in presence of copper salts. Crystals, melting at 147°. Boils at 267°. Sublimes in leaflets. Readily soluble in water, alcohol, and ether. Yields quinone on oxidation. When oxidised in the presence of primary amines or phenols it gives indamines and indophenols, these on heating produce safranines. By heating it with sulphur to 150°–180°, it is converted into diamino-thiodiphenylamine (leucothionine, Lauth's white)

$$NH\begin{cases}C_6H_3(NH_2)\\C_6H_3(NH_2)\end{cases}S$$
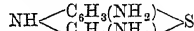
which, when oxidised with ferric chloride, yields thionine (Lauth's violet)

$$N$$
$$H_2N\cdots S\cdots NH,HCl$$
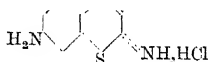
The latter colouring matter may also be obtained by the simultaneous oxidation of p-phenylenediamine and sulphuretted hydrogen by ferric chloride in aqueous solution (Lauth, Compt. rend. 82, 1441; Bull. Soc. Chim. 25, 422; Bernthsen, Annalen, 230, 108). If dimethyl-p-phenylenediamine $C_6H_4(NMe_2)(NH_2)$ is substituted for p-phenylenediamine in the foregoing reaction, tetramethylthionine (methylene blue) is formed (v. Methylene blue).

Tolylene-diamines (Diaminotoluenes)
$$C_6H_3(CH_3)(NH_2)_2.$$
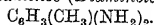
All the six possible compounds are known. Their physical constants are as follows :—

	M.pt.	B.pt.
1-Methyl-2 : 3-diaminobenzene	61°	255°
2 : 4		283°–285°
2 : 5	64°	273°
2 : 6	103°	—
3 : 4	88°	265°
3 : 5		284°

Only two of these, however, are of technical importance.

AMINO-ACIDS. 135

Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$ (1, 2, 4). Obtained by the reduction of the corresponding idnitrotoluene. Sparingly soluble in cold, readily soluble in boiling water, in alcohol, and in ether. Forms crystalline salts. As the two amino groups in this compound are in the meta- position to one another, it is an analogue of *m*-phenylenediamine, which it resembles in many of its reactions : thus 2 : 4-tolylenediamine may either wholly or in part replace the *m*-phenylenediamine used in the manufacture of phenylene-brown, producing colouring matters the shade of which is redder than that of ordinary phenylene-brown.

Tolylenediamine $C_6H_3(CH_3)(NH_2)_2$ (1, 2, 5) is obtained by the reduction of the corresponding *m*-nitro-*o*-toluidine $C_6H_3(CH_3)(NH_2)(NO_2)$ (1,2,5) with tin and hydrochloric acid (Beilstein and Kuhlberg, Annalen, 158, 350 ; Ladenburg, Ber. 11, 1651). Formed along with *o*-toluidine when the aminoazotoluene prepared from *o*-toluidine is treated with the same reducing agent :
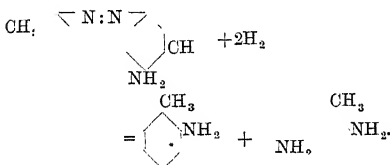
The two bases may be separated by fractional distillation (Nietzki, Ber. 10, 832). This reaction is utilised in preparing the mixture of *o*-toluidine and γ-tolylene-diamine which, after the addition of a second molecule of a monamine (either aniline or *o*- or *p*-toluidine), yields on oxidation safranine. On a large scale the aminoazotoluene is reduced with iron turnings and hydrochloric acid. Crystallises in colourless rosettes of tabular crystals. Readily soluble in water, alcohol, and ether, sparingly soluble in benzene. Yields on oxidation toluquinone $C_6H_3(CH_3)O_2$.

Other diamines of this series are—

Xylylene diamines :
1.3-dimethyl, 2.4-diaminobenzene, m.p. 64°.
1.3- ,, 4.6 ,, ,, ,, 104°.
1.3- ,, 2.5 ,, ,, ,, 77°.
Diaminotrimethylbenzenes : diamino- pseudo-cumenes :
1.2.4-trimethyl, 5.6-diaminobenzene, m.p. 90°.
1.2.4- ,, 3.6 ,, ,, m.p. 78°.
Diamino mesitylene :
1.3.5-trimethyl, 2.4-diaminobenzene, m.p. 90°.
Similar diamines have been prepared from naphthalene and other hydrocarbons.

TRIAMINES, TETRAMINES, AND PENTAMINES.

Very few of these substances are known. Their properties are similar to those of other substances containing the amino group.
1.2.3-*triaminopropane* ; b.p. 190° (Curtius, J. pr. Chem. 1900, 62, 232).
2.3.5-*triaminohexane* (Morelli and Marchetti, Atti del Accad. Lin. 1908, [5] 17, 1, 250).
The three modifications of triaminobenzene are all known.
1.2.3-*triaminobenzene* ; m.p. 103° ; b.p. 336°.
1.2.4-*triaminobenzene* is formed by reduc-

tion of *o-p*-dinitraniline or of chrysoidine. On oxidation it gives triaminophenazin.
1.3.5-*triaminobenzene* is only known in the form of its salts.
1.2.3.4. and 1.2.4.5-*tetraminobenzenes* prepared by the reduction of oximes and nitro compounds, have been isolated as their sparingly soluble sulphates (Nietzki and Schmidt, Ber. 1889, 22, 1648 ; Nietzki, Ber. 1887, 20, 2114).
Pentaminobenzene has been obtained as the hydrochloride with 3 molecules of HCl, by reduction of triaminodinitrobenzene (from tribrombenzene and ammonia). Pentaminotoluene has been similarly obtained.
Reduction of triaminotrinitrobenzene gives pentaminobenzene (Palmer and Jackson, Ber. 1888, 21, 1706 ; Palmer and Grindley, *ibid.* 1893, 26, 2304). M. B. T.

AMINO-ACIDS. The amino-acids may be conveniently described under the two headings (*a*) *Aliphatic Amino-acids*, and (*b*) *Aromatic Amino-acids*.

Aliphatic Amino-acids. The amino-fatty acids are of great physiological importance, many of them occurring in plant and animal organisms. They are products of proteid degradation, and may be obtained from proteins by heating with hydrochloric acid or baryta water. The general methods in use for preparing these acids are :

(i.) By treating the monohalogenated fatty acids with ammonia :
$$CH_2Cl \cdot COOH \rightarrow CH_2(NH_2)COOH.$$
Chloracetic acid.   Glycine.
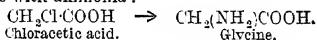
(ii.) By heating the cyanhydrin of an aldehyde or ketone with ammonia and then hydrolysing the product, whereby an α-amino-acid is produced :
$$CH_3 \cdot CH{<}^{CN}_{OH} \rightarrow CH_3 \cdot CH{<}^{CN}_{NH_2}$$
$$\rightarrow CH_3 \cdot CH(NH_2)CO_2H.$$
Alanine.
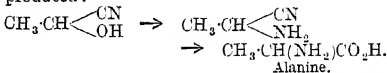
(iii.) By the reduction of the cyanofatty acids with nascent hydrogen (Zn and HCl or by heating with HI)
$$CN \cdot CO \cdot OH + 2H_2 = CH_2(NH_2)CO_2H.$$
Cyanoformic acid.
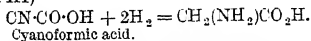
The amino-fatty acids are crystalline bodies with usually a sweet taste, and are readily soluble in water. They are amphoteric, *i.e.* feeble bases and feeble acids. Important members are glycine, alanine, phenylalanine, tyrosine, leucine, and valine, serine, cystine. tryptophane, histidine, arginine, lysine, aspartic acid, and glutaminic acid, which are described under their respective headings (*v.* also PROTEINS).

(*b*) **Aromatic Amino-acids.** A true aromatic amino-acid such as anthranilic acid, contains both the amino and the carboxyl- groups united to carbon atoms in the benzene ring. Isomeric with these are acids which contain the amino group or the carboxyl- group or both, introduced into fatty side chains, the last two classes being really substituted fatty acids.
The general methods in use for preparing aromatic amino-acids are :
(i.) By reducing the corresponding nitro-acids :
$$C_6H_4(NO_2)COOH(1:2) \rightarrow C_6H_4(NH_2)COOH(1:2)$$
o-nitrobenzoic acid.   Anthranilic acid.
(ii.) By treating the halogen esters with
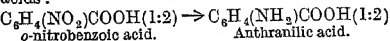
potassium phtalimide and hydrolysing the product with hydrochloric acid at 200°.

The aromatic amino-acids are used in the preparation of azo-dyestuffs (*q.v.*).

o-Aminobenzoic acid. Anthranilic acid

$$C_6H_4(NH_2)CO_2H \quad (1:2).$$

It was first obtained by heating indigo with caustic potash (Fritzsche, Annalen, 39, 83). It may be prepared by the reduction of *o*-nitrobenzoic acid with tin and hydrochloric acid (Beilstein and Kühlberg, Annalen, 163, 138), or with zinc and sodium bisulphite (Goldberger, Chem. Zentr. 1900, ii. 1014; *v.* also Preuss and Binz, Zeit. angew. Chem. 1900, [16] 385 and Bad. Anil. u. Soda Fab. Eng. Pat. 18319; J. Soc. Chem. Ind. 1900, 774); by heating *o*-chlorbenzoic acid and ammonia at 125° under pressure (Fabw. Meister, Lucius und Brüning, D. R. P. 145604; Chem. Soc. Abst. 1904, i. 50); by treating phthalimide with bromine and caustic potash (Hoogewerff and van Dorp, Ber. 1891, Ref. 966; Bad. Anil. und Soda Fab. D. R. P. 55988; Frdl. ii. 546; Amsterdamsche Chininefabrik. Eng. Pat. 18246; J. Soc. Chem. Ind. 1891, 831); by boiling phthalhydroxylamic acid, formed by treating phthalic anhydride with hydroxylamine, with caustic soda or sodium carbonate (Cie. Par. de Coul. d'Aniline, Fr. Pat. 318050; J. Soc. Chem. Ind. 1902, 1392; Farbw. Meister, Lucius und Brüning, Eng. Pat. 1982, D. R. P. 136788; Basler Chemische Fabw.; D. R. PP. 130301, 130302); by reducing sulphanthanilic acid electrolytically or with sodium amalgam (Kalle and Co. D. R. P. 129165; Chem. Zentr. 1902, i. 1138; D. R. P. 146716; Chem. Soc. Abst. 1904, i. 159); by treating *o*-nitrotoluene with concentrated alcoholic or aqueous alkali (Bad. Anil. und Soda Fab. D. R. P. 114839; Chem. Zentr. 1900, ii. 1892); and by heating isatoic acid with concentrated hydrochloric acid (Kolbe, J. pr. Chem. [2] 30, 124).

Anthranilic acid is of great commercial importance, as it is one of the intermediate products in the manufacture of synthetical indigo. It crystallises in colourless plates, m.p. 145°, and is readily soluble in alcohol or water. It condenses with formaldehyde, forming compounds which are of use in the preparation of indigo (Heller and Fiesselmann, Annalen, 324, 118; Bad. Anil. und Soda Fab. D. R. PP. 117924, 158090, 158346; J. Soc. Chem. Ind. 1905, 615). Reduction with sodium amalgam in hydrochloric acid solution yields *o*-aminobenzylalcohol (Langguth, Ber. 1905, 2062). Concentrated hydriodic acid decomposes it at 200° into ammonia, carbon dioxide, aniline and benzoic acid (Kwisda, Monatsh. 12, 427); whilst nitrous acid converts it in aqueous solution into salicylic acid. Anthranilic acid is employed in the preparation of azo- dyestuffs (*q.v.*) (*v.* also Bayer and Co. D. R. PP. 58271, 60494, 60500, 86314; Frdl. iii. 614, *et seq.* iv. 795).

The methyl ester of anthranilic acid occurs in Neroli oil (oil of orange flowers) (Walbäum, J. pr. Chem. 1899, 59, [6-7] 350). It is prepared by heating anthranilic acid with methyl alcohol and hydrochloric acid (Erdmann, Ber. 1899, 1213; D. R. P. 110386) or from acetylanthranilic acid, methyl alcohol and mineral acids (Erdmann, D. R. P. 113942; Chem. Zentr. 1900, ii. 831). It is a crystalline solid, m.p. 24·5°,

b.p. 135·5° (15 mm.). The ethyl ester melts at 13° and boils at 136°–137° (13·5 mm.): at 266°–268° (corr.) (Frankel and Spiro, Ber. 1895, 1684). Aminobenzoic acid alkamine esters (*v. p*-aminobenzoic acid).

Anthranil

$$C_6H_4{<}\!\!\!\begin{array}{c}CO\\|\\NH\end{array} \quad \text{or} \quad C_6H_4{<}\!\!\!\begin{array}{c}CH\\|\\N\end{array}\!\!\!{>}O$$
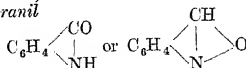
is the anhydride or lactam of anthranilic acid, its constitution being still under discussion. It is prepared by treating the dimercury derivative of *o*-nitrotoluene (obtained by suspending *o*-nitrotoluene in water and heating it with freshly precipitated mercuric oxide and caustic soda) with concentrated hydrochloric acid and decomposing the product with water (Kalle and Co. Fr. Pat. 370522; D. R. P. 194364; J. Soc. Chem. Ind. 1907, 278; 1908, 713); by heating *o*-nitrotoluene with caustic soda to 170° (Kalle and Co. D. R. P. 194811; Chem. Soc. Abstr. 1908, i. 786); by the reduction of *o*-nitrobenzaldehyde with aluminium amalgam (Brühl, Ber. 1903, 3634); and by the oxidation of *o*-aminobenzaldehyde with a neutral solution of Caro's persulphuric acid (Bamberger and Demuth, Ber. 1903, 829; 2042).

Anthranil is an oil, readily volatile in steam, possesses a peculiar odour, and boils at 210°–213°. It dissolves in alkalis to form salts of anthranilic acid and on treatment with acetic anhydride yields acetylanthranilic acid.

m-Aminobenzoic acid. Benzamic acid $C_6H_4(NH_2)CO_2H$ (1 : 3), is prepared by reducing *m*-nitrobenzoic acid with ammonium sulphide and subsequently precipitating the acid with tartaric acid (Holleman, Rec. Trav. Chim. 1902, [ii.] 21, 60; *v.* also Gerland, Annalen, 91, 188). It is a colourless crystalline solid, m.p. 174°; sparingly soluble in cold, readily so in hot water. Reduction with sodium amalgam in hydrochloric acid yields *m*-aminobenzyl alcohol (Langguth, Ber. 1905, 2062). Concentrated hydriodic acid transforms it into ammonia and benzoic acid (Kwisda, Monatsh. 12, 428). *m*-Aminobenzoic acid is used in the preparation of azo-dyestuffs (*q.v.*) (Bayer and Co., D. R. PP. 58271, 59081, 60494, 60500, 63104, 64529, 69445, 74198, 74516, 78493, 86314; Frdl. iii. 614 *et seq.*, 777 *et seq.* : iv. 793, 795; Ges. f. Chem. Ind., D. R. P. 76127; Frdl. iii. 746). Aminobenzoic acid alkamine esters (*v. p*-aminobenzoic acid).

p-Aminobenzoic acid $C_6H_4(NH_2)CO_2H$ (1 : 4), is prepared by the reduction of *p*-nitrobenzoic acid with ammonium sulphide (Fischer, Annalen, 127, 142) or with tin and hydrochloric acid (Beilstein and Wilbrand, Annalen, 128, 164). It is a colourless crystalline solid, m.p. 186°–187°, readily soluble in water, alcohol, or ether. Strong hydrochloric acid at 180° converts it into aniline and carbon dioxide (Weith, Ber. 1879, 105) and hydriodic acid at 200° into ammonia, carbon dioxide, and benzoic acid (Kwisda, Monatsh. 12, 428). *p*-Aminobenzoic acid is used in the preparation of azo- dyestuffs (*q.v.*) (Bayer and Co. D. R. PP. 58271, 60494, 60500, 86314; Frdl. iii. 614 *et seq.* ; iv. 795; Ges. f. Chem. Ind., D. R. P. 76127; Frdl. iii. 746).

Many complicated alkyl- and alkamine esters of the aminobenzoic acids have been prepared and they are claimed to be valuable anæsthetics

(Farbw. Meister, Lucius, and Bruning, D. R. PP. 170587, 172301, 172447, 172568, 179627, 180291, 180292, 194748, Eng. Pat. 17162, Fr. Pat. 361734, U. S. Pat. 812554 ; J. Soc. Chem. Ind. 1906, 607 ; 1907, 434 ; Chem. Soc. Abstr. 1906, i. 845 *et seq.* ; 1907, i. 923 ; 1908, i. 638 ; Merck, D. R. P. 189335 ; J. Soc. Chem. Ind., 1908, 471 ; Bayer and Co. D. R. PP. 211801, 218389, Eng. Pat. 4321 ; J. Soc. Chem. Ind. 1909, 854 ; Chem. Zentr. 1910, i. 782 ; Fritzsche, Eng. Pat. 2020, Fr. Pat. 398259, D. R. P. 213459 ; J. Soc. Chem. Ind. 1909, 814).

4-*Amino-o-toluic acid* $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 4 : 2) ; m.p. 196°. Obtained by the reduction of 4-nitrotoluic acid with tin and hydrochloric acid (Jacobsen and Wierss, Ber. 1883, 1959).

5-*Amino-o-toluic acid* $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 5 : 2) ; m.p. 153°, is obtained by the reduction of 5-nitrotoluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1884, 164).

6-*Amino-o-toluic acid* $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 6 : 2). Method of preparation as above ; m.p. 191° (J. and W. *l.c.*).

2-*Amino-m-toluic acid* $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 2 : 3). Method of preparation as above ; m.p. 132° (Jacobsen, Ber. 1881, 2354), 172° (Jürgens, Ber. 1907 4409).

4-*Amino-m-toluic acid* (*Methylanthranilic acid*) $C_6H_3 \cdot CH_3$ $(NH_2) \cdot CO_2H$ (1 : 4 : 3). Obtained by reduction of 4-nitro-*m*-toluic acid with tin and hydrochloric acid (Jacobsen, Ber. 1881, 2354) or by treating *p*-methylisatoic acid with concentrated hydrochloric acid (Panaotovic, J. pr. Chem. [2] 33, 62) ; m.p. 172° (Ehrlich, Ber. 1901, 3366), 175° (Findeklee, Ber. 1905, 3533).

6-*Amino-m-toluic acid* $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 6 : 3) ; m.p. 167°. Obtained by reduction of 6-nitro-*m*-toluic acid (Beilstein and Kreusler, Annalen, 144, 147).

2-*Amino-p-toluic acid* $C_6H_3 \cdot CH_3 \cdot (NH_2) \cdot CO_2H$ (1 : 2 : 4) ; m.p. 164°-165°. Method of preparation as above (Ahrens, Zeitsch. f. Chemie, 1869, 104).

3-*Amino-p-toluic acid* (*Homo-anthranilic acid*) $C_6H_3 \cdot CH_3(NH_2)CO_2H$ (1 : 3 : 4) ; m.p. 177°. Method of preparation as above (Niementowski and Rozanski, Ber. 1888, 1997 ; Noyes, Amer. Chem. J. 10, 479).

1'-*Amino-o-toluic acid* (*Benzylamine-o-carboxylic acid*) $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ (1 : 2). Obtained by digesting 1 part of *o*-cyanobenzylphthalimide with 4 parts of concentrated sulphuric acid (Gabriel, Ber. 1887, 2231). Crystalline nonvolatile solid.

1'-*Amino-m-toluic acid* (*Benzylamine-m-carboxylic acid* $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ (1 : 3) ; m.p. 215°-218°. By heating at 200° a mixture of 2 grams *m*-cyanobenzylphthalimide and 10 c.c. concentrated hydrochloric acid (Reinglass, Ber. 1891, 2419).

1'-*Amino-p-toluic acid* (*Benzylamine-p-carboxylic acid*) $NH_2 \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ (1 : 4). Method of preparation as above (Günther, Ber. 1890, 1060). Crystalline solid.

2-*Amino-α-toluic acid* (2-*Aminophenylacetic acid*) $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ (1 : 2) is not known in the free state ; all attempts to prepare it result in the formation of its anhydride, oxindole. *Oxindole*

$$C_6H_4 {<}^{CH_2}_{NH}{>}CO$$

is obtained by treating 2-nitro-α-toluic acid with tin and hydrochloric acid (Bayer, Ber.

1878, 583), or by reducing dioxindole with tin and hydrochloric acid, or with sodium amalgam (Bayer and Knop, Annalen, 140, 29). Crystallises in colourless needles ; m.p. 120°.

3-*Amino-α-toluic acid* (3-*Aminophenylacetic acid*) $NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CO_2H$ (1 : 3). Obtained by reducing 3-nitro-α-toluic acid with tin and hydrochloric acid ; m.p. 148°-149° (Gabriel and Borgmann, Ber. 1883, 2065).

4-*Amino-α-toluic acid* (4-*Aminophenylacetic acid*) $NH_2 \cdot C_2H_4 \cdot CH_2 \cdot CO_2H$ (1 : 4). Method of preparation as above (Radziozewski, Ber. 1869, 209) ; m.p. 199°-200° (Bedson, Chem. Soc. Trans. 1880, 92).

α-*Aminophenylacetic acid* $C_6H_5 \cdot CH(NH_2)CO_2H$. Obtained by heating α-phenylbromacetic acid with aqueous ammonia at 100°-110°, Siäckenius, Ber. 1878, 2002) ; m.p. 256° (Tiemann, Ber. 1880, 383). Sublimes without melting at 265° (Elbers, Annalen, 227, 344).

α-AMINO CAPROIC ACID *v.* LEUCINE.

AMINONAPHTHOPHENAZINE *v.* AZINES.

AMINOPHENYLACETIC ACID *v.* AMINO-ACIDS (AROMATIC).

AMINOPHENOPHENANTHRAZINE *v.* AZINES.

α- and **β-AMINOPROPIONIC ACIDS** *v.* ALANINE.

α-AMINO-iso-VALERIC ACID *v.* VALINE.

AMLA (Beng.), **AMLIKA** (Hind.), **AMLIKU** (Ass.), **OWLA** (Mechi), **NELLI** and **TOPPINELLI** (Tam.). A euphorbiaceous Indian tree, *Phyllanthus emblica* (Linn.), the fruits of which (*Emblic myrobalans*) are used in a fresh condition as a laxative, and, when dried, as an astringent (Dymock, Pharm. J. [3] 10, 382). The fruits are also pickled and eaten, and used for tanning and dyeing.

AMMONAL *v.* EXPLOSIVES.

AMMONIA. *Volatile alkali, alkaline air, spirit of hartshorn.* Solutions of ammonia have been known from very early times, but the substance itself was first clearly recognised by Priestley, who obtained it by heating the aqueous solution and collecting the gas, which he termed *alkaline air*, over mercury. Scheele proved that it contained nitrogen ; and Berthollet, and more accurately Austin, demonstrated its real nature, and determined the proportions of its constituents.

Ammonia (or its salts) is found in small quantities in the air, and in most natural water ; in the juice of plants, in most animal fluids, in many soils, and in a few minerals, ochres, clays, marls, &c. Ammonia can be obtained synthetically in small quantity by the passage of electrical discharges through a mixture of nitrogen and hydrogen (Donkin, Pogg. Ann. 21, 281) ; or as nitrite by the action of a strong induction spark on a mixture of nitrogen and water vapour (Thénard, Compt. rend. 76, 983) ; or as chloride by sparking a mixture of hydrogen, nitrogen, and hydrogen chloride (Deville, Compt. rend. 60, 317) ; or by the action of heated spongy platinum, pumice, &c., on a mixture of hydrogen and nitric acid.

For laboratory purposes the gas is usually prepared by heating a mixture of ammonium chloride or sulphate with slaked lime, or by gently warming the concentrated solution, and drying the gas over quicklime. (For the preparation of the chemically pure gas, see Stas, Zeitsch. anal. Chem. 6, 423.)

Ammonia is a colourless gas, having a very pungent characteristic smell, and is poisonous when breathed in quantity, destroying the mucous membrane. It has a sp.gr. of 0·5967 (air = 1), 1 litre of the gas at 0° and 760 mm. weighing 0·7708 gram, and readily liquefies on compression, the critical temperature being 131°, and the critical pressure 113 atm. Liquid ammonia is colourless and very mobile, and has a sp.gr. at 0°·4° of 0·6385 (Dieterici), 0·6388 (Drewes), the coefficient of expansion being very high and increasing rapidly with the temperature. It boils under atmospheric pressure at −33·5°, and freezes to a white crystalline solid at −75° (Faraday), −77° (Brill), the vapour pressure being as follows (Regnault, J. 1863, 70) :—

at −30° 1·14 atm.   at 0° 4·19 atm.
,, −20° 1·83 ,,   ,, 10° 6·02 ,,
,, −10° 2·82 ,,   ,, 20° 8·41 ,,

Its latent heat of evaporation is, with the exception of that of water, higher than that of any known liquid, amounting to about 5000 cal. at 15° and 5600 cal. at its boiling-point, and on this account it is produced commercially in large quantity for employment in freezing machines. In many of its physical properties the liquid resembles water, and it acts as a solvent for a large number of substances.

Ammonia gas burns with difficulty in the air when cold, but inflames more readily on heating, and still more readily in oxygen, giving a greenish-yellow flame of high temperature. In presence of suitable catalysts, such as copper, iron, nickel, and especially platinum, ammonia is oxidised by oxygen at lower temperatures with production of oxides of nitrogen, the manufacture of nitric acid from ammonia by Ostwald's process (Eng. Pat. 698, 1902) being carried out in this manner. A number of the elements, when heated in ammonia gas, yield corresponding nitrides, boron, magnesium ; and titanium being especially active in this respect, whilst the alkali metals give rise to amides. With carbon at temperatures above 750° ammonia is partly dissociated, and partly converted into hydrocyanic acid, the presence of the latter in crude coal gas being largely due to this reaction.

Many salts combine with ammonia to form stable compounds at the ordinary temperature, the ammonia playing the same part as water of crystallisation. It is evolved on heating, liquid ammonia having been first obtained by Faraday, in 1823, by warming the compound with silver chloride 2AgCl,3NH₃, in a sealed tube.

The action of heat upon ammonia has been investigated by Ramsay and Young (Chem. Soc. Trans. 45, 92), Perman (Proc. Roy. Soc. 74, 110 ; 76A, 167), Haber and v. Oordt (Zeitsch. anorg. Chem. 44, 341), and Nernst and Jost (Zeitsch. Elek. 13, 521). Under atmospheric pressure, decomposition commences at temperatures below 500°, its extent increasing rapidly with the temperature, but the speed with which equilibrium is attained between undecomposed ammonia and nitrogen and hydrogen varies greatly according to the nature of the surfaces with which the gases are in contact. Glass is very inactive, but porcelain and many metals and their oxides have a very strong accelerating effect. In presence of the latter decomposition

becomes nearly complete at 630° under atmospheric pressure, but the last traces do not disappear even at 1000°. Conversely, in presence of iron as catalyst, Haber and v. Oordt find that at 1000° traces of ammonia are formed from nitrogen and hydrogen at atmospheric pressure, and Nernst and Jost have found that small quantities are formed at the same temperature under the greater pressure of 50–70 atm. Recently, however, Haber has found that at temperatures of 500°–550° under 200 atm. pressure, in presence of metallic osmium or uranium, nitrogen and hydrogen combine to a considerable extent (see below).

Ammonia gas is very soluble in water, alcohol, ether, and many saline solutions, the aqueous solution (caustic ammonia or *liquor ammoniæ*) being of great commercial importance. One gram of water at 0° and 760 mm. absorbs 1148 c.c. or 0·875 gram of ammonia, at 10° 0·679 gram, at 20° 0·526 gram, at 30° 0·403 gram, and at 100° 0·074 gram (Roscoe and Dittmar, Chem. Soc. Trans. 12, 128 ; Sims, Chem. Soc. Trans. 14, 1 ; see also Perman, Chem. Soc. Trans. 79, 718 ; 83, 1168). In the act of solution much heat is evolved, and according to Thomsen, $NH_3+aq. = 8430$ cals.

The density of aqueous solutions of ammonia of varying strength, according to the determinations of Lunge and Wiernik, is given on p. 139.

The solution is very strongly alkaline, and unites with acids to form the ammonium salts, and it is frequently supposed that the solution contains ammonium hydroxide NH_4·OH, corresponding to NaOH and KOH. The evidence for this view is not altogether conclusive, and the physical properties of the solution at the ordinary temperature are in some respects opposed to the presence of the compound NH_4OH, and in favour of the supposition that the ammonia is dissolved as such. At very low temperatures, however, Rupert (J. Amer. Chem. Soc. 31, 866 ; 32, 748) has shown that two definite hydrates exist, the freezing-point curve of mixtures of ammonia and water in varying proportions showing two well-defined minima at −87° and −94° respectively, the composition at these two points corresponding to the formulæ NH_3,H_2O and $2NH_3,H_2O$. The first-named forms small colourless crystals resembling those of sodium and potassium hydroxide ; and the latter, larger needle-shaped crystals. Whether these are true hydrates or are to be regarded as ammonium hydroxide NH_4OH and ammonium oxide $(NH_4)_2O$, is at present uncertain.

The aqueous solution of ammonia also dissolves many metallic oxides and hydroxides, such as $Ag_2O,Cu(OH)_2$, as well as many salts which are insoluble in water, such as silver chloride and phosphate, and cuprous chloride, and also acts as a solvent for many fats and resins. The solution of cupric hydroxide in ammonia is of considerable commercial importance, as it is a solvent for cellulose, and is used in large quantities in the manufacture of artificial silk.

I. Technical sources of ammonia.[1] Ammonia is formed in nature chiefly during the decay of nitrogenous organic substances, and conse-

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[1] For more complete details, see Lunge's Coal-Tar and Ammonia, chaps. xii.–xv. (Gurney and Jackson, 1909).

quently exists in considerable quantity both in the soil and the atmosphere. Whilst this is of the greatest importance for agriculture, it is only possible in very exceptional cases to utilise this source for the manufacture of ammonium salts, practically the whole of the world's production being obtained by the destructive distillation of nitrogenous organic matter, chiefly coal.

A. *Natural occurrence of ammoniacal compounds in quantity of commercial importance.*— Ammonium carbonate has been found in guano deposits on the West Coast of South America, and has been imported into Europe, a sample imported into Germany in 1848 consisting essentially of ammonium bicarbonate mixed with some insoluble matter. Ammonium sulphate is contained in the Tuscan ' soffioni,' and is there obtained in considerable quantity as a by-product in the manufacture of boric acid. Ammonium chloride, together with sulphate, is sometimes found in the neighbourhood of volcanoes.

B. *Synthetic processes for production of ammonia.*—Very many attempts have been made to effect the manufacture of ammonia from atmospheric nitrogen, and a large number of processes with this object have been patented. Hitherto, however, no method which has been proposed has proved successful on a commercial scale, for although, as stated above, nitrogen and hydrogen combine together to a slight extent to

DENSITY OF AQUEOUS SOLUTIONS OF AMMONIA AT 15° (LUNGE AND WIERNIK).

Sp.gr.	NH_3 p.c.	1 litre contains NH_3 g.	Correction of sp.gr. for $\pm 1°$	Sp.gr.	NH_3 p.c.	1 litre contains NH_3 g.	Correction of sp.gr. for $\pm 1°$
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

form ammonia, when heated together under suitable conditions, the yield at high temperatures is so small that the cost of production would be prohibitive. With many of the methods proposed—such as those of Swindells (Eng. Pat. June 21, 1876), Rickman (Eng. Pat. 3341, 1878), Glover (Eng. Pat. 1890, 1880), Solvay (Bull. Soc. chim. 25, 527), Wagner (Jahresbericht. 1876, 444), Bassett (Eng. Pat. 4338, 1879)—it is very doubtful whether, in fact, any ammonia is produced synthetically, the ammonia obtained being more probably all derived from the nitrogen present in the coal or coke employed in each of these processes. The processes of Johnson (Chem. News, 43, pp. 42, 288), Woltereck (J. Soc. Chem. Ind. 1908, 158, 978 ; Eng. Pat. 2461, 1902 ; 16,504, 1904 ; 8358, 1905), Mond (J. Soc. Chem. Ind. 1889, 505), and Roth (D. R. P. 191914), in which a mixture of nitrogen and hydrogen is passed over various heated catalytic agents, do not appear to have resulted in any commercial yield of ammonia. Haber (Zeitsch. Elek. Chem. 16, 244) has found that when a mixture of 1 vol. of nitrogen and 3 vols. of hydrogen is heated with metallic osmium to 550° under a pressure of 200 atm., a very considerable production of ammonia takes place amounting to 8 p.c. of the mixed gas, and although osmium is too scarce and expensive for technical use, it may be replaced by metallic uranium with good results. With a small apparatus constructed to allow of the circulation of the mixed gas under this pressure over uranium heated to

about 500°, and cooling between each passage of the gas over the metal, Haber has synthesised ammonia at the rate of about 90 grams per hour, the ammonia separating out on cooling under these conditions as a liquid. Larger plant is now being erected by the Badische Anilin und Sodafabrik.

Attempts to effect the synthesis by the passage of the silent discharge and of sparks through the mixture of nitrogen and hydrogen have also failed to effect a sufficient yield of ammonia. Patents for this type of process have been taken out by Young (Eng. Pat. 1700, 1880), Müller and Geisenberger (Eng. Pat. 1481, 1879 ; 1592, 1879), the Société d'Azote (D. R. P. 17070), Nithack (D. R. P. 95532), West-Deutsche Thomasphosphatwerke (D. R. P. 157287 and 179300), Gorianoff (Fr. Pat. 368585), Hooper (U.S. Pat. 791194), and Cassel (D. R. P. 175480); see also Briner and Mettler (Compt. rend. 144, 694), and Davies (Zeitsch. physikal. Chem. 64, 657). A similar lack of commercial success has hitherto attended the efforts to produce ammonia by combining atmospheric nitrogen with elements which readily form nitrides, such as boron, titanium, magnesium, and calcium, and subsequent conversion of the nitride into ammonia by the action of steam ; patents in this respect having been taken out by Bassett (Eng. Pat. 4338, 1897), Lyons and Broadwell (U.S. Pat. 816628), Wilson (Eng. Pat. 21755, 1895), Mehner (Eng. Pat. 12471, 1895 ; 2654, 1897 ; 28067, 1903), Kaiser (Eng. Pat. 26803, 1905), Borchers and Beck (D. R. P. 196323), and Roth (D. R. P. 197393).

C. Production from cyanides.—It has long been known that nitrogen combines at high temperatures with carbon and alkalis with production of cyanides, and many attempts have been made during the last fifty years to manufacture cyanides in this manner and to convert these subsequently into ammonia by the action of superheated steam. The large demand for cyanides themselves, resulting from their employment in the extractions of gold from the mine tailings, and the fact that at present nitrogen, in the form of cyanide, commands a higher price than in the form of ammonia, has made such processes of no value for ammonia production under existing conditions, and in fact, at the present time, the opposite process of converting ammonia into cyanides is carried on to a large extent. The methods proposed, so far as they relate to cyanide production, will be discussed under that heading, but one method may be here mentioned, namely, the manufacture of calcium cyanamide, $Ca : N \cdot C : N$, according to Frank and Caro's process (J. Soc. Chem. Ind. 1908, 1093), by the action of nitrogen on heated calcium carbide, this being simultaneously a cyanogen and an ammonia derivative (*v. Cyanamide*, art. NITROGEN, ATMOSPHERIC, UTILISATION OF). This substance may readily be converted into ammonia by the action of superheated steam, but it is for the most part directly employed on the land as a nitrogenous manure.

D. Ammonia from urine, sewage, and animal excreta.—Urine is not merely the oldest, but for centuries was the only source for obtaining ammonia compounds on a commercial scale.

It is stated that sal-ammoniac made from it was an article of commerce as early as 1410, and that the Jesuit Sicard in 1720 saw the manufacture of it in the Delta of the Nile. In Egypt sal-ammoniac was made by burning camels' dung and collecting the sublimate. Putrefied urine (in which the urea has passed into ammonium carbonate) has been used for centuries, and to a certain extent is still used by dyers as a source of ammonia for scouring wool and other purposes. The methodical working up of urine collected in large quantities, or of sewage for obtaining ammonia therefrom, has been carried out in the neighbourhood of some large towns, *e.g.* Paris, but only a very small quantity of ammonia in comparison with the enormous quantity excreted is actually obtained in this way.

Normal urine contains per litre from 20 to 35 grams urea (carbamide), which after a short time is changed into ammonium carbonate under the influence of a micro-organism. An adult man produces from 22 to 37 grams urea per 24 hours, together with a little uric acid, corresponding to 12·5–21 grams NH_3 per day, or between 9 and 17 lbs. per annum. If all the ammonia obtainable from London urine were recovered this would amount to 100,000 tons of ammonium sulphate per annum.

Owing to the now almost universal adoption of the removal of sewage by means of water, the dilution of the ammonia in the combined sewage is so great that its recovery is hardly practicable, but with concentrated pan sewage, recovery of ammonia is carried on in a few places, especially in Paris. A large number of patents have been taken out for the recovery of ammonia both from sewage and also from the more concentrated sludge deposited in the collecting tanks at the sewage works, among which may be mentioned Duncan (D. R. PP. 27148, 28436), Young (Eng. Pat. 3562, 1882), Bolton and Wanklyn (Eng. Pat. 5173, 1880), Gesellschaft für Wasserabklärung, Berlin (D. R. P. 161166), Butterfield and Watson (Eng. Pat. 19502, 1905), Taylor and Walker (U.S. Pat. 603668).

In Paris there are daily 2200 cubic metres (say tons) of urine and night soil taken out of the fosses, and treated by various processes. In the Bilange process the sewage is mixed with milk of lime and allowed to settle, the liquid portion is worked for ammonia, the muddy deposit (containing a great many albuminoid matters) is heated by steam, passed through filter-presses and sold as manure. In the Kuentz process the muddy deposit is mixed with a reagent prepared by treating a mixture of bauxite, natural phosphate of lime, and hydrated oxide of iron with hydrochloric acid. The resulting mass is passed through filter-presses ; the cakes remaining in these contain all the phosphoric acid (10–12 p.c.) as dicalcic phosphate, precipitated by ammonium carbonates ; the iron has absorbed the sulphur compounds, and the alumina has modified the albuminous and slimy matters which would have impeded the filtration. The percentage of nitrogen in these cases is 3–3·5.

Ketjen (Zeitsch. angew. Chem. 1891, 294) also reports a successful recovery of ammonia from concentrated sewage by distillation with lime at Amsterdam.

E. *Ammonia from guano, &c.*—Whilst the ammonia obtainable from excreta is mostly lost for immediate recovery, as it quickly passes away into the water, the soil, or the air, there are a few exceptions to this rule presented by the deposits of birds' excrements on some desert islands, and a few similar cases. In this ' guano,' ammonia salts exist already preformed, and ammonia can be formed from other nitrogenous substances contained therein by heating guano with lime (as patented by Young in 1841), but this process is not remunerative, since the direct manurial value of guano is much superior to that of the ammonia salts obtainable therefrom.

F. *Manufacture of ammonia by the destructive distillation of nitrogenous organic matter.*—The total quantity of ammonia commercially produced by all of the methods described above is at present almost negligible, nearly the whole of the world's supply of ammonia and its salts being obtained as a by-product in the course of other manufactures in which nitrogenous organic matter is subjected to the process of destructive distillation. By far the greatest proportion is obtained in the manufacture of illuminating gas, power gas, or coke from coal, and in the distillation of shale for the production of shale oil. A considerable amount is also recovered from the gases evolved from blast-furnaces where coal is used as fuel, and smaller quantities from the distillations of bones, horn, and other animal refuse, and also from the residue obtained from beet-root molasses.

The total production of ammonia in the United Kingdom, calculated as sulphate, for the years 1907–8–9, is shown in the following table, the figures for 1889 being also given to indicate the increase in production during the past 20 years. The statistics are taken from the Annual Reports of the Chief Alkali Inspector :—

	1889	1907	1908	1909
Gas works	. 87,000	165,474	165,218	164,276
Iron works	. 5,500	21,024	18,131	20,228
Shale works	. 22,000	51,338	53,628	57,048
Coke ovens	. —	53,572	64,227	82,886
Producer gas and other carbonising works	. 3,000	21,873	24,024	24,705
	117,500	313,281	325,228	349,143

The world's production for 1907 is given in Mineral Industry, 16, 31, as follows :—

Great Britain	331,220 metric tons (2204 lbs.)
Germany	287,000 ,,
United States	81,400 ,,
Holland and Belgium	55,000 ,,
France	52,900 ,,
Other European countries	88,000 ,,
	895,520 ,,

Of the German production, only 30,000 tons were produced from gas works, the remainder being derived chiefly from coke ovens.

Coal always contains nitrogen in greater proportion than is present in fresh vegetable matter, this being probably due to the remains of animals inhabiting the coal-forming forests and swamps. The total percentage of nitrogen found in the coal usually varies between the limits of 0·9 and 2·0 p.c. ; thus Tidy (Lunge's Coal Tar and Ammonia, 4th ed. p. 872) found in Welsh coal 0·91 p.c., in Lancashire coal 1·25 p.c., and in Newcastle coal 1·32 p.c., whilst Foster (Inst. Civ. Eng. 77, iii. 23) found in Welsh anthracite 0·91 p.c., in English coals 1·66–1·75 p.c., and in Scotch cannel 1·28 p.c. Schilling (J. Gasbel, 1887, 661), using the Kjeldahl method of estimation, obtained from Westphalian coal 1·50 p.c., from Saar coal 1·06 p.c., from Silesian coal 1·35 p.c., from Bohemian coal 1·36 p.c., from Saxon coal 1·20 p.c., from Boldon (Durham) coal 1·45 p.c., from Pilsener cannel 1·49 p.c., and from Bohemian lignite 0·52 p.c. McLeod (J. Soc. Chem. Ind. 1907, 137) analysed 80 samples of Scotch coals and cannels, and found percentages of nitrogen varying from 0·91 to 1·87, and averaging 1·43.

The world's production of coal in 1909 amounted to about 950,000,000 tons, containing on the average probably some 1·3 p.c. of nitrogen, which, if the whole were recovered as ammonia, would represent an output of about 48,000,000 tons of ammonium sulphate per annum. In fact, however, the production, as shown by the above figures, only amounts to about $\frac{1}{20}$ of this quantity. Fully 90 p.c. of the coal is consumed in such a manner that the recovery of the nitrogen is impracticable, and where the processes in use are such that ammonia is recovered, only a relatively small proportion of the nitrogen is actually obtained in the form of ammonia, for reasons discussed later in considering the different manufactures in which it is produced.

(*a*) *Production of ammonia in the manufacture of coal gas, and of coke in by-product coke ovens.*— The carbonisation of coal in retorts for the manufacture of illuminating gas for general distribution at present yields the largest contribution of ammonia, but the output from this source is being rapidly approached by that obtained in the analogous process of carbonising the coal in ovens for the manufacture of hard metallurgical coke. Formerly the great bulk of such coke was manufactured in beehive ovens, in which case no by-products were recovered, but these are now being rapidly replaced by by-product recovery ovens, the quantity of ammonium sulphate obtained from this source in the United Kingdom having increased from about 10,000 tons in 1899 to 83,000 tons in 1909.

In both industries, however, only a portion of the nitrogen of the coal is recovered in the form of ammonia, the remainder being distributed in the coke, as nitrogenous compounds in the tar, as cyanide in the gas and ammoniacal liquor, and as free nitrogen in the gas. The relative proportion of the nitrogen obtained in the different forms varies considerably, being dependent both on the nature of the coal and on the conditions of carbonisation ; the rate at which the latter proceeds, and especially the temperature employed have a marked influence. At low temperatures, such, for example, as are employed in the manufacture of ' coalite ' (about 450°), a very large proportion of the nitrogen remains in the coke, but with higher temperatures, although more nitrogen is given off from the coke primarily in the form of ammonia, this is partly converted into hydrocyanic acid by the action of incandescent carbon

and partly dissociated into its elements, the latter being especially the case when the volatile products as well as the residual coke are strongly heated. The maximum yield of ammonia, when carbonising in horizontal retorts appears to take place at a temperature of about 900°–950°, but with vertical retorts heated to much higher temperatures, a greater yield of ammonia is claimed, owing to the fact that the volatile products are not raised to so high a temperature before escaping from the retort.

The following tables, which give figures obtained over a long period of working in gas-works and coke ovens respectively, probably represent a fair average of the distribution of the nitrogen in the two industries under modern conditions, although doubtless in different works considerable variations from these figures occur. The gas-works figures are given by McLeod (J. Soc. Chem. Ind. 1907, 137) as the result of working at the Provan Gas Works, Glasgow, and the coke-oven figures by Short (J. Soc. Chem. Ind. 1907, 551) for the working of Otto-Hilgenstock Coke Ovens, using Newcastle coal.

	Gas works	Coke ovens	
Nitrogen in coke	58·3	43·31	p.c. of total
„ in tar	3·9	2·98	„
„ as ammonia	17·1	15·16	„
„ as cyanide	1·2	1·43	„
„ as free nitrogen in the gas	19·5	37·12	„

McLeod does not appear, however, to include in his cyanide figures the hydrocyanic acid removed from the gas during condensation, allowance for which would probably raise the cyanide figure to about 1·5 p.c.

In both gas and coke-oven works the ammonia is recovered by cooling the gas, when tar and aqueous vapour condense, the condensed water removing a large portion of the ammonia and other gaseous impurities from the gas, and the remainder being recovered by washing the cooled gas with water. Recently, also, in coke-oven works, processes have been adopted in which the ammonia is directly recovered from the hot gas by washing with sulphuric acid after removal of the tar. Methods for manufacturing ammonium sulphate direct from the crude gas, in which the sulphuretted hydrogen present is simultaneously oxidised to form the necessary sulphuric acid, have been described by Feld (Eng. Pat. 3061, 1909) and Burkheiser (Eng. Pat. 20920, 1908; 21763, 1908; 17359, 1910), but the processes are still (1910) in the experimental stage.

The various apparatus employed and methods of working are described in the articles on Gas (Coal) and Coke. The yield of ammonia in both gas works and coke ovens, calculated as sulphate, amounts usually to 20–25 lbs. per ton.

Many attempts have been made to increase the proportion of nitrogen converted into ammonia, but none applicable to these two industries has had any success. Cooper's lime process (Eng. Pat. 5713, 1882), in which lime is added to the coal before carbonisation, was tried in many works, and abandoned, as, although a greater yield of ammonia was obtained, the gain in this respect was more than counterbalanced by the loss due to depreciation in the quality of the resulting coke.

(b) *Production of ammonia in the manufacture of producer gas from coal.*—In the manufacture of producer gas from carbonaceous fuel (see GAS, PRODUCER) by the introduction of limited amounts of air and steam into the incandescent fuel, the whole of the carbon of the latter is gasified together with the nitrogen it contains. Where the quantity of steam added is limited, so as to ensure that the gas produced shall only contain small percentages of carbon dioxide, the temperature of the producer is such that almost the whole of the ammonia formed from the nitrogen is dissociated into its elements as fast as it is produced. If, on the other hand, a large excess of steam is employed, the temperature of the producer is so much lowered that the greater part of the ammonia escapes decomposition, and may then be recovered from the gas evolved. The latter contains much larger percentages of hydrogen and carbon dioxide than that obtained by the use of smaller quantities of steam, but is still capable of economic employment, especially in gas engines. The process is therefore now largely adopted for producers using bituminous fuel, especially in the Mond Gas plant, in which up to about 75 p.c. of the nitrogen in the coal is recovered as ammonia. This is usually obtained direct as sulphate by washing the crude gas with dilute sulphuric acid, and subsequent evaporation and crystallisation of the solution obtained; the sulphate thus produced has, however, generally a yellow or brownish colour, due to the presence of small amounts of tarry matter.

The employment of steam, except in very limited quantity, is impracticable in the carbonisation of coal in gas works and coke ovens, as the chief products required in those industries are gas of relatively high illuminating power and calorific power, or good coke, or both; and the addition of steam in such quantity as materially increases the yield of ammonia, effects so large a depreciation in the quality of gas and coke produced that the loss in these respects far outweighs any increased revenue obtained from the additional quantity of ammonia formed.

(c) *Production of ammonia from shale.*—In the distillation of Scotch bituminous shales for the production of shale oil (see PARAFFIN), ammonia is also evolved, and is recovered in a similar manner to that employed in gas works. In this case also the introduction of steam (and also of limited quantities of air) during the distillation has the effect of largely increasing the percentage of nitrogen recovered as ammonia. The objections to the method which hold in the case of the gas industry do not apply in the shale-oil manufacture, as the chief product, the shale oil, is not materially affected by the use of steam, and the coke formed is in any case of little value. The gas produced, even when steam is used, is sufficiently good for the purpose for which it is used, namely, for heating the retorts. The addition of steam for increasing the yield of ammonia was, in fact, first worked out to practical success in this industry, chiefly by Young and Beilby (Eng. Pat. 1587, 1881; 2164, 1881; 4284, 1881; 1377, 1882; 5084, 1882; see also Beilby, J. Soc. Chem. Ind. 1884, 216), its application in the case of carbonisation of coal in producers for the same purpose being of rather later date.

(d) *Ammonia from blast furnaces.*—Where coal is used as fuel in blast furnaces for cast-iron production, the waste gases contain considerable quantities of ammonia and tarry matters, which are now largely recovered from the gas, the latter, after purification, being employed in gas engines. In most English districts, the coal available is not sufficiently hard for use in the furnaces, and hard coke is used, the employment of coal being confined chiefly to the West of Scotland and to North Staffordshire, where coal of sufficient hardness can be obtained. The recovery of the tar and ammonia is effected by cooling and washing in a similar manner to that employed in gas works, the apparatus being suitably modified to allow for the fact that the tar and ammonia are much more diluted with other gases, and that large quantities of dust are mechanically carried along with the gas from the blast furnace. Processes for the washing of the gas with dilute sulphuric acid do not appear so far to have been permanently successful, and the same is true of the process of Addie (Eng. Pat. 4758, 1882 ; 3246, 1883), in which the gas was mixed with sulphur dioxide and passed through a scrubber fed with water, the resulting solution of ammonium sulphite being oxidised to sulphate by injection of air.

The yield of ammonium sulphate obtained from blast furnaces is very similar to that obtained in gas works and from coke ovens, namely from 20 to 25 lbs. per ton of coal.

(e) *Ammonia from peat.*—Vast deposits of peat exist in many places, especially in Ireland and Prussia, and as this contains a good deal of nitrogen, amounting in some cases to 4 p.c. of the dry peat, many attempts have been made to recover this nitrogen as ammonia. The great difficulty in the way has been the very large quantity of water contained in the peat, which is costly to remove, and hitherto very little ammonia has been put on to the market from this source. Of the earlier attempts that of Grouven (D. R. PP. 2709, 13718, 18051) is of interest, inasmuch as this represents one of the first attempts to increase the yield of ammonia by injection of steam during distillation, but although prolonged experiments were made with the process, it was ultimately abandoned. Lencauchez suggested the use of peat in gas producers with subsequent ammonia recovery, and patents relating to the matter were taken out by Ruderer, Loe, and Gumbart (D. R. P. 53844), Kuntze (Eng. Pat. 9052, 1891), and Pieper (Eng. Pat. 28190, 1896).

More recently Woltereck (Eng. Pat. 16504, 1904 ; 28963, 1906 ; 28964, 1906) has patented a process for recovering ammonia and other products from peat, and works for carrying out the method have been erected near Carnlough Harbour, in the North of Ireland. In his process, the wet peat is placed in a generator, and burned in a current of air and steam, regulated so as to keep the temperature of the generator very low and at the same time to effect almost complete combustion of the peat, no attempt being made to obtain a combustible gas. The products, in addition to the waste gases, are chiefly small quantities of tarry matter of the paraffin series, acetic acid and ammonia, the first being removed by treating the hot gases with high boiling oils, the gas

then passing through hot milk of lime to absorb the acetic acid, and finally through sulphuric acid to recover the ammonia as sulphate. (It is claimed that not only is a quantitative yield of ammonia obtained from the nitrogen of the peat, but that some ammonia is also formed synthetically from the nitrogen of the air used.) Details of the results on the manufacturing scale have not yet been published.

Frank and Caro, in conjunction with the Mond Gas Co. (Zeitsch. angew. Chem. 1906, 1569), find that peat containing 50 p.c. of water may be employed in place of coal in the Mond Gas plants, with production of gas suitable for gas engines, and a yield of about 90 lbs. of ammonium sulphate per ton of dry peat.

(f) *Ammonia from bones, horn, leather, hair, skins, and other animal refuse.*—In the distillation of bones for the manufacture of bone charcoal (animal charcoal, or ' char '), used especially in sugar refining, large quantities of ammonia are formed, together with tar rich in pyridines, known as ' Dippel's oil.' The carbonisation is frequently carried out, especially in France and Germany, by heating the bones in open pots placed in a furnace, in which case the tar and ammonia are so largely diluted with hot furnace gases that their recovery is rendered very difficult. In this country generally, and to an increasing extent elsewhere, the carbonisation is effected in closed retorts, and the tar and ammonia recovered in accordance with the usual gas works practice, the yield of ammonia being equivalent to about 50–60 lbs. of sulphate per ton of dry bones.

Other animal refuse, such as wool, hair, skin, waste leather, &c., is sometimes carbonised in a similar way, the residue being employed as manure, and the ammonia recovered from the gases. Sometimes, however, these materials are simply heated in cylinders in a current of steam, which renders them friable and capable of ready disintegration, when they are directly employed as manure. A further proposal is to utilise the nitrogen by heating the dried refuse with concentrated sulphuric acid, whereby the nitrogen is converted quantitatively into ammonium sulphate, as in the well-known Kjeldahl method of estimating nitrogen.

(g) *Ammonia as a by-product in the beet-root sugar industry.*—During the evaporation of beet-root juice, small amounts of ammonia are evolved, which Vibrans (D. R. P. 15513) has proposed to collect. Much larger amounts can, however, be obtained by the distillation of the ' vinasse,' *i.e.* the residue left after fermenting the sugar remaining in the molasses, and distilling off the alcohol produced. This contains nitrogenous bases, especially betaïne, and on dry distillation yields ammonia and trimethylamine. Vincent (Chem. News, 39, 107) carried out the distillation with the primary object of obtaining trimethylamine and from the latter methyl chloride, but the ammonia was simultaneously recovered as sulphate. The residue from the distillation is rich in potassium salts, and is employed as a manure or worked up into pure salts. Other patents dealing with the recovery of ammonia by distillation of vinasse are those of Ernst (D. R. P. 13871), Lederer and Gintl (D. R. P. 17874), and Meyer (Eng. Pat. 17347, 1887). Bueb (Eng. Pat. 7175, 1895;

26259, 1898; see also Ost, Zeitsch. angew. Chem. 19, 609) utilises the vinasse for the production of both ammonia and cyanides, the latter being the product especially aimed at. In his process the vinasse is carbonised in retorts in the ordinary manner, and the gases, which contain ammonia and trimethylamine, but little hydrocyanic acid, are then passed through a highly heated brickwork chamber, the ammonia being only slightly affected, whilst the trimethylamine is converted chiefly into hydrocyanic acid. The resulting gases, containing about 7 p.c. of ammonia and 7 p.c. of hydrocyanic acid, are passed through sulphuric acid to recover the ammonia as sulphate, and the gas freed from ammonia employed for the manufacture of cyanide.

II. **Properties and Composition of Ammoniacal Liquor.** The ammoniacal liquor obtained by the washing and cooling of the gases produced by destructive distillation, is, after separation from tar by settling, a liquid having a colour from pale yellow to dark brown, and smelling strongly of ammonia, sulphuretted hydrogen, and also of phenols. Its specific gravity usually varies from 1·01 to 1·03. In the coal-gas manufacture, the liquor is usually obtained in three stages, viz. (1) the hydraulic main liquor, formed during the cooling of the gas to temperatures of 50°–60°, which is usually weak (0·5–1·0 p.c. of NH_3), owing to the lessened solubility of ammonia at that temperature; (2) the condenser liquor, produced in the subsequent cooling of the gas to atmospheric temperature, which is more concentrated (2–3·5 p.c. of NH_3); and (3) the scrubber and washer liquor, formed by washing the cooled gas to effect complete removal of the ammonia, the strength of which varies considerably, and depends largely on the construction of the washing plant, and the supervision of the working. The first two products together form the ' virgin liquor,' *i.e.* solution produced from the water formed by the condensation of the steam always present in the crude gas; but the liquor from all sources is usually collected together with the tar in a common storage well or wells. Frequently the weak hydraulic main liquor is used, after cooling, in the preliminary washers or scrubbers, thereby effecting a further partial removal of the ammonia, and becoming simultaneously concentrated, but for the complete removal of the ammonia the gas must be washed with fresh water in the final scrubber. In coke-oven works the conditions prevailing in these respects are very similar generally to those in gas works.

The quantitative composition of the ammoniacal liquor varies considerably, not only in that obtained at different stages of the process, but also in the average liquor obtained, being dependent on the nature of the coals carbonised, the conditions of carbonisation, and the construction and working of the condensing and scrubbing plant. The qualitative composition varies but little; the primary products formed in the liquor are ammonium chloride, sulphides, carbonates, and cyanide, produced by the action of the ammonia solution on the acid constituents of the crude gas, viz. hydrochloric acid, sulphuretted hydrogen, carbon dioxide, and hydrocyanic acid. The strongly acid hydrochloric acid is absorbed in the earlier stages of

the cooling, chloride being only present to any extent in the hydraulic main and condenser liquor, but the total quantity of ammonia present is insufficient to remove the whole of the remaining acid gases, which are separated later by special purification processes. Other ammonium salts are, however, produced in the liquor by secondary reactions; thus the sulphide is oxidised by the oxygen always present in the crude gas, and later by the oxygen of the air to which it is exposed during storage, yielding polysulphides, thiosulphate, sulphate, and possibly sulphite. The cyanide reacts with the polysulphide, forming thiocyanate, and possibly also with thiosulphate, forming thiocyanite and sulphite, so that polysulphide is rarely if ever found in the liquor. Small quantities of ferrocyanide are also sometimes formed by the action of ammonium cyanide on the ironwork of the apparatus. In addition, the liquor always contains small quantities of pyridine, and considerable amounts of substances derived from the tar, especially phenols.

From the point of view of the subsequent working up of the ammoniacal liquor, it is important to distinguish between the amount of ' volatile ' and ' fixed ' ammonia present. The former represents the ammonia present as sulphide, carbonate, and cyanide, and in combination with the phenols, the term being given because the ammonia in this form is completely dissociated and volatilised by simply boiling the solution; whereas that present as chloride, sulphate, thiosulphate, and thiocyanate is not evolved to any material extent under these conditions, and is therefore termed 'fixed' ammonia. For its recovery it is necessary to add to the liquor a sufficient amount of a stronger alkali to combine with the whole of the above-named acids present. The 'fixed' ammonia in the average liquor usually amounts to from 20 to 25 p.c. of the whole, but the proportion is much higher in the hydraulic main and condenser liquor.

The table on p. 145 gives the results of a number of analyses of ammoniacal liquor from gas-works, coke-ovens, shale-works, and iron-works, made by Linder, on behalf of the Chief Alkali Inspector, and published in the annual reports of the latter. In addition an analysis is also given of the liquor obtained in low-temperature carbonisation as practised in the coalite manufacture, and two analyses of German gas-works liquor, by Mayer and Hempel (J. Gasbel, 1908, 428). (For methods of analysis, *see* Linder (Alkali Inspector's Report, 1909, 15), and Mayer and Hempel (*l.c.*).) In these analyses the whole of the carbon dioxide and sulphuretted hydrogen present is calculated as the normal carbonate and sulphide respectively, and in Linder's analyses the difference between the total sulphur and that present as sulphide, sulphate, and thiocyanate is calculated as ammonium thiosulphate.

The existence of free ammonia (or its hydroxide) is a point on which considerable difference of opinion exists. The above analytical results appear to show that in the case of average stored liquor, the quantity of acids present, including phenol, is usually sufficient to combine with the whole of the ammonia

but at the same time it is very probable that some of the salts, especially the sulphides and carbonates, undergo hydrolytic dissociation into acid and free ammonia or its hydroxide in the solution. With the hydraulic main liquor, formed at temperatures mostly above 60°, the acids found are insufficient to combine with the whole of the ammonia, some of which must therefore be present in the free state. The existence of free ammonium cyanide in the liquor has also frequently been denied, but more perfect methods of analysis have shown that this is undoubtedly often present in small quantity even in stored gas-works liquor, and that in coke-oven liquor, which is usually only stored for a short time before working up, the amount may be considerable. The presence of cyanide is objectionable, as it increases the amount of hydrocyanic acid in the waste gases from the manufacture of ammonium sulphate (*see* below).

III. **Valuation of Ammoniacal Liquor.** In this country, for technical purposes, the strength of the ammoniacal liquor is mostly expressed in terms of 'ounce-strength,' this figure representing the number of ounces avoirdupois of pure sulphuric acid required to neutralise the ammonia contained in 1 gallon of the liquor, and for statistical purposes or sale, the volumes of liquor are usually converted into the equivalent volume of liquor of 10-oz. strength. In order to convert these figures into the more generally

COMPOSITION OF AMMONIACAL LIQUOR.

	Gas works					Coke ovens	Blast furnaces		Shale works	Coalite works	
—	Average of five samples of stored liquor.— English works	Stored well liquor.— German works	Hydraulic main liquor.— English works	Hydraulic main liquor.— German works	Condenser liquor.— English works	Average of nine samples of liquor	Liquor from coolers only	Liquor from washers only	Average liquor from st'orage well.	Average liquor circulated through washers to get up strength	—
Volatile ammonia	1·929	1·406	0·721	0·291	3·247	0·841	0·191	0·362	0·873	1·547	grams per 100 c.c.
Fixed ,,	0·613	0·309	0·306	0·288	0·221	0·102	0·008	0·009	0·032	0·170	,,
Total ,,	2·542	1·715	1·027	0·579	3·468	0·943	0·199	0·371	0·905	0·717	,,
Ammonium sulphide $(NH_4)_2S$	0·862	0·276	0·276	0·073	0·768	0·466	nil	?	0·098	0·230	,,
,, carbonate $(NH_4)_2CO_3$	5·000	3·526	1·320	0·475	8·810	1·960	1·104	?	2·870	6·360	,,
,, chloride NH_4Cl	1·120	0·738	0·838	0·722	0·459	0·217	0·006	?	0·015	0·106	,,
,, sulphate $(NH_4)_2SO_4$	0·202	0·023	?	0·023	?	0·032	0·009	?	0·016	0·054	,,
,, thiosulphate $(NH_4)_2S_2O_3$	0·173	0·123	?	0·143	?	0·041	0·002	?	0·090	0·407	,,
,, thiocyanate NH_4CNS	0·528	0·182	0·047	0·100	0·070	0·043	0·003	0·003	nil	0·335	,,
,, cyanide NH_4CN	0·036	0·003	0·034	0·003	0·070	0·070	nil	0·003	nil	⅞nil	,,
,, ferrocyanide $(NH_4)_4Fe(CN)_6$	0·038	0·088	0·019	0·019	0·030	nil	nil	nil	nil	⅞nil	,,
Authority	Linder	Mayer and Hempel	Linder	Mayer and Hempel	Linder	Linder	Linder	Linder	Linder	Linder	

The quantity of phenols present in gas-works liquor usually varies from 0·1 to 0·35 grams per 100 c.c. (Skirrow, J. Soc. Chem. Ind. 1908, 58).

familiar ones of grams per 100 c.c., the 'oz.-strength' figures must be multiplied by 0·217, and conversely, to convert figures representing grams per 100 c.c. into oz.-strength, the former must be multiplied by 4·61.

For approximate purposes the ammonia content of the liquor is frequently estimated from the density, it being found that each 1° Twaddell corresponds roughly to 2-oz. strength. This approximation is sufficient for such purposes as the control of the daily working of the washers and scrubbers on the works, but quite unsuitable for purposes where fair accuracy is desired, as a liquor showing 5°Tw., for example, may vary in actual content from 8- to 12-oz. strength, as against the supposed 10-oz. For any but the roughest purposes, ammonia is

estimated by the usual method of distilling a known volume, after addition of alkali to decompose the fixed salts, collecting the distillate in excess of standard acid, and titrating the unused acid with standard alkali. The liquid must not be distilled to dryness, as otherwise the thiocyanates may be decomposed with formation of ammonia, giving too high results.

IV. **Working up of Ammoniacal Liquor.** In the earlier days of the utilisation of gas liquor, this was simply neutralised with sulphuric or hydrochloric acid, and the resulting solution evaporated, but the products obtained were very impure, containing tarry matter and thiocyanate, and the escaping gases, especially the sulphuretted hydrogen, created great nuisance. At present the ammonia is almost

invariably recovered from the liquor in the first instance by distillation. Formerly, also, in many cases, only the volatile ammonia was recovered, as this could be obtained without addition of alkali, the fixed ammonia being run off with the waste liquor; but this procedure is now becoming exceptional, the fixed ammonia, except in the case of some small plants, being also mostly recovered by addition of the necessary alkali. On account of its cheapness, lime is almost always employed for this purpose, but in some small plants, caustic soda is used, for although the cost of the latter is much greater, this is held by some makers to be compensated for in such plants by the fact that the stills run much longer without cleaning.

The plant employed in the distillation has been of various types; at first an intermittent process of distilling the liquor in externally fired boilers was adopted, the distillation being continued until the whole of the volatile ammonia

was expelled with the steam. Addition of lime to drive off the fixed ammonia was rarely practised with such plants, owing to the formation of thick deposits of lime salts on the heated boiler plates. These plants have now been almost entirely superseded by continuous column stills, constructed on the general principle of the Coffey still, the intermittent system being now employed only in very small works or in special cases, such as the distillation of liquors containing very large quantities of fixed ammonia, in which case the addition of the necessary amount of lime renders the liquid so thick that these must be stirred by mechanical agitators to effect complete recovery of the ammonia. The annual report of the Chief Alkali Inspector for 1909 shows that in the various districts into which the United Kingdom is divided for administration purposes under the Alkali Act, the proportion of liquor distilled by intermittent stills varies from about 7 p.c. to *nil*,
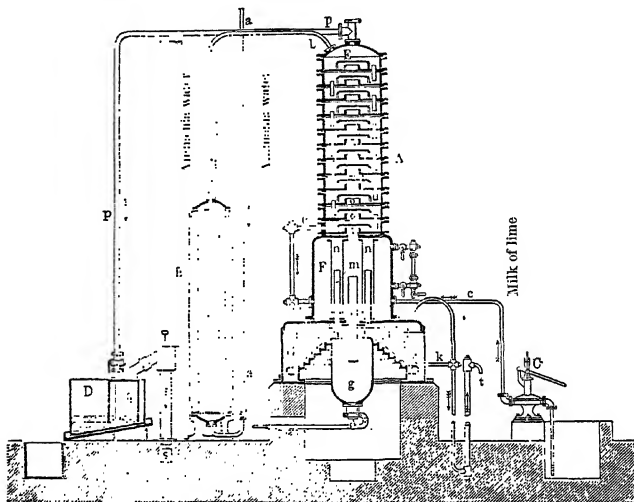
Fig. 1.

and probably averages over the whole country from 1 to 2 p.c.

For the purpose of heating the stills, three methods have been employed : (1) external firing ; (2) by means of internal coils through which steam is passed ; and (3) by blowing live steam through the stills. The first plan gives a high fuel consumption, as well as trouble from lime deposits on the heated portions of the still ; and of the other two methods the use of live steam is the most economical in fuel consumption, and is therefore now almost invariably adopted.

The ammonia evolved on distillation is converted at once either into ammonium sulphate, concentrated gas liquor, pure aqueous ammonia, or liquefied ammonia. The remaining salts of commercial importance, namely, ammonium chloride, carbonate, and nitrate, are now rarely manufactured directly from the ammonia as evolved from the stills, but are obtained either from ammonium sulphate or aqueous

ammonia previously prepared from the gas liquor. Much the largest proportion of the liquor is converted into sulphate, the demand for this salt being greatest, owing to its employment as a nitrogenous manure. The method of manufacture of this salt will therefore be described first, followed by that of the other commercially important ammonia derivatives.

Ammonium sulphate.—A description of the different forms of intermittent still formerly adopted for obtaining the ammonia in the liquor, but now seldom used, may be found in Lunge's Coal Tar and Ammonia 4th ed. Of the continuous stills, those of Grüneberg and Blum (D. R. P. 33320) and of Feldmann (Eng. Pat. 3643, 1882) will be described, more recent forms differing from these only in detail and not in general principles. In the manufacture of sulphate, the volatile ammonia is first driven off, lime being then added to the liquor to liberate the fixed ammonia,

the combined gases evolved being passed through sulphuric acid.

The apparatus of Grüneberg and Blum is shown in Fig. 1, as arranged for the manufacture of sulphate. A is the still, B the gas-liquor heater or economiser, C the lime pump, and D the saturator charged with acid for absorption of the ammonia. The gas liquor enters the economiser B by means of pipe a, and is heated by the hot waste gases from the saturator, and passes thence by the pipe b to the top of the column E of the still. This column is divided into a number of compartments by horizontal division plates, the liquor flowing downwards from compartment to compartment by the overflow pipes, the admitted steam travelling upwards in the reverse direction through the central pipes o, covered by hoods having serrated edges, which compel the steam to bubble through the liquor in each compartment, thus driving off the ' volatile ' ammonia and also the volatile acids present, viz. carbon dioxide, sulphuretted hydrogen, and hydrocyanic acid.

The lime vessel F, into which milk of lime is pumped by means of pump C and pipe c, serves to expel the fixed ammonia, and the boiler G, with its stepped cone, serves to boil the liquor in thin sheets, by means of the steam coil d, and thus to set free the last portions of ammonia. In B the first heating of the liquor takes place by means of the hot vapours from the saturator D, which ascend through the bell q, the pipe s, and the inner pipes of B, while the liquor, arriving at a, rises up in B. It then enters through b into the dephlegmating column E, and finds its way downward from chamber to chamber, till it gets into the lime vessel F. From here it overflows by pipe f into the sludge-catcher g, overflows here again all round at hh, and runs over the cone i downwards from step to step ; from the pipe k it is discharged continuously and quite spent to the overflow t. The steam travels in the opposite way—namely, along the steps of cone i, upwards in pipe m, and through n into the lime vessel F. From here the mixed steam and ammonia vapours ascend into the column E, and traverse this from chamber to chamber, and ultimately leave it by the pipe p. This pipe enters the saturator D, charged with sulphuric acid. The sulphuretted hydrogen, carbon dioxide, &c., collecting in the bell q, are led through the flue s into the economiser B, where they give up their heat to the gas liquor, and lose their steam in the shape of condensed water. Ultimately they are conveyed away by a pipe not shown in the diagram for treatment to prevent nuisance, the methods adopted for the purpose being described below.

In the apparatus of Feldmann (D. R. P. 21708), Fig. 2, the gas liquor, after having passed through the ordinary rectifying column A, flows into a vessel B, into which milk of lime is pumped by G in regular intervals, whilst the whole is kept agitated by steam injected into the mixture. The liquor, after having deposited most of the lime, flows into a second column C, where the ammonia set free by the lime is distilled off : the spent liquor runs away continuously through q, and the gases and vapours pass over by pipe h into the first column BA, which serves both for retaining the water and for driving off the vola-tile ammonium salts contained in the crude

gas liquor. The economiser J, and the saturator B, with the gas-bell F, require no special explana-tion.
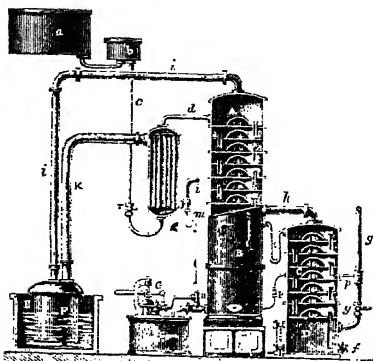
Fig. 2.

In more recent types of still, only a single column is usually employed, the lime being introduced into one of the compartments of the lower portion of the still, which may be made of larger size for this purpose, the hood being also more deeply sealed to effect more vigorous agitation. The mixture of liquor and lime then passes through the lower compartments of the still, constructed in a similar manner to those above. A still of this type, manufactured by the Berlin Anhaltische Maschinen Actien-Gesellschaft, is shown in Fig. 3.
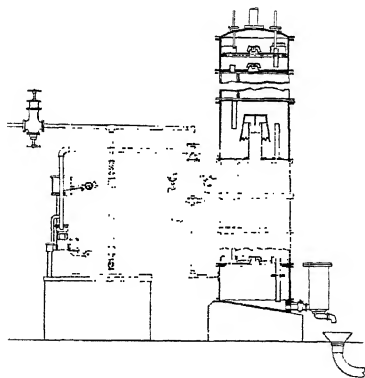
Fig. 3.

Other modifications relate chiefly to im-provements in mechanical details, and in making the parts more accessible for cleaning, especially in the portions of the still where lime is present. Thus Wilton (Eng. Pat. 24832, 1901) replaces the central pipe for the steam and circular hood, by a narrow opening extending over nearly the full diameter of the still, and covers this with an inverted trough having serrated edges, which can readily be removed for cleaning from

a small manhole at the side. Scott (Eng. Pat. 3987, 1900 ; 11082, 1901) has patented a process in which the whole of the plant is kept under vacuum, whereby considerable economy of fuel is claimed. The plant and method of working are described by Ballantyne (J. Gas Light. 82, 869).

Absorption of the ammonia in sulphuric acid. —The gases from the still, consisting chiefly of ammonia steam, carbon dioxide, sulphuretted hydrogen, and small quantities of hydrocyanic acid, are conveyed to the saturator (D in Fig. 1, E in Fig. 2) charged with sulphuric acid. This is constructed either of solid lead throughout, or of wood or iron lined with lead, the gases being conducted in by means of a perforated leaden pipe which distributes them over a large area in the saturator and keeps the liquid thoroughly agitated. In some cases, dilute sulphuric acid is used, this being removed and replaced by fresh acid when nearly neutralised. The solution, after settling, is concentrated and crystallised, the mother liquor being returned to the saturator. The dilute solution of ammonium sulphate obtained by direct washing of the crude gas with acid, as in the Mond Gas process, is evaporated and crystallised in a similar way. In most cases, however, when distilling gas liquor, a much stronger acid (of about 140°Tw.) is used which soon becomes saturated, after which the ammonium sulphate crystallises out as formed, and is removed by various means, fresh acid being run in to replace that removed as sulphate. Two types of saturator are employed, (*a*) partly open, (*b*) closed. A common construction of the former type is shown in Fig. 4, the gases

FIG. 4.

entering by the pipe *b* perforated as shown, and bubbling through the acid, the waste gases being led off by the pipe *c* ; the sulphate accumulates on the floor of the saturator. The front of the saturator is open, and separated from the closed portion by the sealing curtain *a*, which does not reach to the bottom, and enables the attendant to remove the sulphate periodically by fishing with a perforated ladle, the crystals being placed on a lead-lined drainer fixed so that the mother liquid flows back to the saturator.

When sufficiently dry, the product is placed into stock, or it may be at once dried by a centrifugal machine.

In place of ' fishing,' the sulphate may be periodically or continuously removed from the saturator by means of a steam-ejector, which forces it together with much liquor on to the drainer, thence into a centrifugal machine, the mother liquor in either case returning to the saturator.

With a closed saturator other means of removing the sulphate are adopted, a representative of this type being the Colson saturator,

FIG. 5.

the bottom of which consists of an inverted cone, to the apex of which is fixed a right-angled bend, closed by a simple valve, consisting of a copper disc pressed against the flange of the outlet pipe by a screw clamp. During working this is opened to a sufficient extent to allow the sulphate to fall out almost as soon as it is formed.

The ammonium sulphate thus obtained usually contains from 24 to 25 p.c. of ammonia, equivalent to about 93–99 p.c. of pure ammonium sulphate. It usually contains from 0·1 to 0·5 p.c. of free sulphuric acid, the remainder consisting of moisture and small quantities of insoluble matter. The salt produced with modern plant has mostly a white or greyish-white colour, discolouration by tarry matter being now of rare occurrence with continuous stills, if the liquor is properly separated from tar by settling previous to distillation. When pyrites sulphuric acid is employed, the resulting sulphate may be coloured yellow or brown, by arsenic sulphide, which depreciates its value, and makers therefore prefer to use acid obtained from brimstone or spent oxide. In many cases, however, pyrites acid is used, and the arsenic sulphide which rises as a scum to the surface of the liquid in the saturator removed as it forms, or preferably the acid is previously treated with a portion of the waste gases from the saturator, the sulphuretted hydrogen in which precipitates the arsenic as sulphide, the latter being removed before the acid enters the saturator.

In some cases the sulphate assumes a blue colour on standing in the air, owing to the formation of traces of Prussian blue. From the researches of Forbes Carpenter and Linder (Chief Alkali Inspector's Report, 1905, 51), it appears that this is mostly due to local alkalinity occurring in some portion of the liquid in the saturator, in which case hydrocyanic acid is absorbed at that point, and, with the traces of iron always present, forms ammonium ferrocyanide ; the latter, on exposure to the air, oxidises, forming Prussian blue. Priming of the still, resulting in the introduction of ferrocyanides and thiocyanates into the saturator, has a similar effect, but the production of the blue salt often occurs in absence of priming. Its formation is best avoided by maintaining the liquid hot and of sufficient acidity, and arranging that the passage of the gas shall effect a thorough mixing of the liquid in the saturator, so as to prevent the occurrence of local alkalinity.

Waste products in the manufacture of Ammonium Sulphate.—Three waste products are formed in the process : (*a*) the effluent liquor ; (*b*) the aqueous condensate from the cooling of the waste gases ; (*c*) the waste gases. The effluent liquor is run into settling tanks, where it deposits suspended lime salts, and becomes cooled. The clarified liquor is sometimes run into the sewers, but as it contains large quantities of lime salts (especially thiocyanate and phenols), this is frequently not permitted, and its disposal is often a matter of great difficulty. In gas works it is sometimes got rid of by employing it to quench the hot coke from the retorts, and in some cases it is even evaporated to dryness. Fowler (Alkali Inspector's Report, 1907, 51) allows the liquor, after considerable dilution, to pass through coke filters inoculated with sewage bacteria, which, if gradually accustomed to the liquor, oxidise the thiocyanates and phenols, yielding a fairly pure effluent, and this may be employed for dilution of the fresh liquor going on to the filter. Radcliffe (Eng. Pat. 10075, 1905) removes the thiocyanates by precipitating as cuprous thiocyanate with copper sulphate in presence of sulphurous acid, the latter being obtained by burning a portion of the waste gases. Grossmann (Eng. Pat. 20387, 1905 ; 7932, 1907 ; J. Soc. Chem. Ind. 1906, 411) has also described a process for avoiding the production of waste liquor and recovery of the ferrocyanide and thiocyanates present in it.

The avoidance of the production of waste liquor altogether is an especial object in the process of the Otto-Hilgenstock Coke Oven Co. (Eng. Pat. 12809, 1908) now being adopted in some coke-oven works. In this the gas from the ovens is treated for the removal of tar at temperatures above that at which water condenses, and then passed directly through sulphuric acid ; the aqueous condensate obtained in the subsequent cooling of the gas is free from ammonia, and only contains small amounts of impurity, and it is claimed that no difficulty is experienced in disposing of it. Wilton (Eng. Pat. 16355, 1909) has patented a somewhat similar process with the same object.

The aqueous condensate obtained by cooling the waste gases is a very noxious-smelling liquid, and is hence termed ' devil-liquor.' It contains sulphuretted hydrogen, pyridines, and similar substances, and hydrocyanic acid, and is also difficult to dispose of. The hot condensate from the liquor-heater or economiser is less objectionable than that obtained in the further cooling of the waste gases, which contains much more sulphuretted hydrogen ; but if the latter is returned to the pipe conveying the hot condensate and the waste gases from the economiser, most of the sulphuretted hydrogen is driven off again into the waste gases, and the combined liquor, after cooling, may be mixed with the effluent from the stills without increasing the difficulty of dealing with the latter (Broadberry, J. Gas Light. 69, 345).

The waste gases, after cooling, consist chiefly of carbon dioxide, sulphuretted hydrogen, and smaller quantities of hydrocyanic acid, as well as strongly smelling empyreumatic vapours derived from the tar. With coke-oven liquors, which often contain considerable quantities of cyanide, the amount of hydrocyanic acid may be considerable, necessitating additional care in dealing with it owing to the poisonous nature of the gas. In many cases the gases are burned under the boiler or other furnaces, and discharged with the products of combustion from the chimney : or the gases may be burned separately and the resulting sulphur dioxide absorbed by passing the products through a limestone tower down which water is passing, yielding a solution of calcium bisulphite, or through scrap-iron towers, when a solution of ferrous sulphate is formed (Wilton, Eng. Pat. 15468, 1901). With small and medium-sized plants, the sulphuretted hydrogen and hydrocyanic acid are mostly removed by oxide of iron, in a similar manner to that employed for purifying coal gas. In place of purifying boxes, conical heaps of oxide of iron on a concrete floor are now much used, the gas being introduced from the bottom at the centre of the heap ; the spent oxide obtained is saleable for its sulphur content. The sulphuretted hydrogen may also be precipitated with metallic salts, and where sulphuric acid is also made, the gases are burned and passed into the chambers, thus recovering the sulphur as sulphuric acid. A considerable proportion of the waste gas is converted into sulphur by the Claus process (Eng. Pat. 3606, 1882 ; 5070, 1883 ; 5958, 1883), also used on the large scale in the Chance sulphur-recovery process. By this method, sufficient air is mixed with the gas to react with the sulphuretted hydrogen in accordance with the equation $2H_2S + O_2 = 2H_2O + 2S$, and the mixture passed through a kiln containing heated ferric oxide, the sulphur formed being deposited in cooling chambers, and the residual gases passed through a small limestone tower and oxide-of-iron purifier to remove any sulphur dioxide or sulphuretted hydrogen remaining. The sulphur obtained is not very pure, owing to tarry matters, &c., present in the gases treated.

Manufacture of Caustic Ammonia (Liquor Ammoniae) and of Liquefied Ammonia.—The pure aqueous solution of ammonia was formerly manufactured by distilling ammonium sulphate with lime in intermittent stills provided with mechanical arrangements for stirring the somewhat thick cream, but it is now usually made by the direct distillation of gas liquor, with suitable purification of the gas evolved from the stills, which is then dissolved in water. In addition

to the pure aqueous solution, a crude solution containing sulphide, and sometimes carbonate, is also largely manufactured, this being cheaper and equally applicable to many purposes, especially in the manufacture of soda by the ammonia-soda process, and for the preparation of other ammonium salts. This crude product is termed 'concentrated gas liquor,' two kinds being manufactured, the one containing from 16 to 18 p.c. of ammonia, with both sulphide and carbonate present, and the other from 18 to 26 p.c. of ammonia, with some sulphide but little or no carbonate.

In the manufacture of the first-named liquor, the gases from the stills, worked as in the manufacture of the sulphate, pass through a reflux condenser, to remove some of the steam present, and then through a direct condenser, the gases from which are washed with water. Working in this manner, it is not practicable to obtain a greater strength of ammonia than 16–18 p.c., as with higher concentrations stoppages occur in the condenser from crystallisation of ammonium carbonate. For the preparation of the more concentrated gas liquor, the vapours from the still, after passing the reflux condenser, are led through a washer containing milk of lime, which removes practically the whole of the carbon dioxide and some of the sulphuretted hydrogen, a liquor being then obtained by condensation usually, containing 22–26 p.c. of ammonia, and a little sulphide, but usually free from carbonate.

Pure Caustic Ammonia.—In the manufacture of pure aqueous ammonia from gas liquor, a sufficient quantity of lime must be employed to remove the whole of the acid constituents of the liquor, including the carbon dioxide and sulphuretted hydrogen. For the complete removal of the latter the use of a decided excess of lime is necessary, and owing to the hydrolysis of calcium sulphide even excess of lime does not remove the last traces of sulphuretted hydrogen, which is eliminated by other reagents. The addition of the large amount of lime required in the stills themselves during the distillation of the liquor, gives rise to much trouble from blockage in the latter, and it is therefore mostly found preferable to effect the removal of those two gases by passing the still vapours through lime washers. Much economy in the use of lime results if the liquor, previous to distillation, is subjected to a preliminary heating to 70°–80° (Hills' process), at which temperature a large proportion of the carbon dioxide and sulphuretted hydrogen are evolved, accompanied by only small amounts of ammonia, the latter being recovered by washing the evolved gases with water or weak ammoniacal liquor, or, where the manufacture of sulphate is carried on simultaneously, the gases evolved may be passed direct to the sulphuric-acid saturator, along with the gases from the stills used in that process.

The preheated liquor is distilled as in the case of the sulphate process, and the gases evolved, after traversing a reflux condenser, pass through a set of two or three washers, containing cream of lime, to remove carbon dioxide and sulphuretted hydrogen, the partly used lime being run back into the stills to effect the decomposition of the fixed ammonium salts, and recovery of ammonia from the cream. To

ensure the removal of the last traces of sulphuretted hydrogen, ferrous sulphate solution is sometimes added to the last lime washer, the ferrous hydroxide formed by the action of the lime retaining the gas as ferrous sulphide, or, according to Pfeiffer (J. Gasbel. 1900, 89), a small final washer containing caustic soda solution is added. Solutions of sodium permanganate or ammonium persulphate may also be used (Foucar). The gases then pass through a series of scrubbers charged with wood charcoal, which remove the strongly smelling empyreumatic substances derived from the tar, and, in some cases additional purification in this respect is effected by passing the gas through a fatty or high-boiling mineral oil. The resulting purified gas is then led into distilled water, and thus converted into solution of any desired strength up to about 36 p.c. The charcoal scrubbers must be renewed as soon as their activity becomes lessened, the spent material being revivified by heating in closed retorts.

Technical caustic ammonia is usually clear and colourless, and contains only small quantities of pyridine and empyreumatic substances. When these are present in larger quantity, owing to defective action of the charcoal filters, the liquid assumes a yellowish colour on keeping. Its strength is ascertained from its specific gravity. A table showing the specific gravity of different concentrations is given on p. 139.

Liquefied Ammonia.—The liquefied gas, stored in steel cylinders, is now largely produced and employed for refrigeration purposes. It is manufactured from the gas obtained and purified as described for the manufacture of the pure aqueous solution, but instead of passing it into water, it is well dried, and then compressed by suitable pumping machinery. The commercial liquid usually contains small amounts of water, pyridine, and lubricating oil, and traces of other substances, but is now sold, in many cases, as of guaranteed 99·9 p.c. purity.

Ammonium Chloride (Muriate of Ammonia or Sal-ammoniac).—This salt has been manufactured in a similar manner to that employed for the sulphate, by passing the gases from the stills into hydrochloric acid, but as lead is attacked under these conditions, the saturator must be constructed of stoneware or similar material, which has many disadvantages. It is now usually made by neutralising hydrochloric acid with concentrated gas liquor, and evaporating and crystallising the resulting solution, or by evaporating a solution of ammonium sulphate and sodium chloride in equivalent proportions ; the sodium sulphate formed separates out during concentration as the monohydrate, which is removed by ' fishing,' leaving finally a concentrated solution of ammonium chloride, which is purified by crystallisation.

It is also manufactured by neutralising " galvanisers' pickle " (which consists chiefly of ferrous chloride) with ammonia, and by the action of ammonium carbonate (or of ammonia and carbon dioxide) on calcium chloride solution, the latter being obtained in large quantity as a by-product in the ammonia-soda manufacture, and in that of potassium chlorate ; the solutions of ammonium chloride obtained in either case

are evaporated and crystallised after removal of the precipitated substances.

Ammonium chloride is frequently further purified by sublimation, the sublimed product being known as *sal-ammoniac*. In this country the operation is carried out in large iron pots externally heated and covered with a similar concave iron plate on which the sublimate (sal-ammoniac) forms. This is detached at the end of the operation, the surface adhering to the iron, which is always discoloured, being removed previous to sale. In France the discolouration with iron is avoided by using earthenware pots, but the product is more expensive, owing to the fact that the pots are destroyed at each operation.

The commercial crystallised salt is white or only slightly discoloured, whilst the sublimed material has a fibrous structure, and frequently contains small amounts of iron. It is employed in pharmacy, soldering, galvanising, dyeing, and calico-printing, and in small quantities for many other purposes.

Ammonium Carbonate (Sal-Volatile).—The commercial product sold under this name consists of a mixture of ammonium bicarbonate $NH_4 \cdot HCO_3$ with ammonium carbamate $NH_2 \cdot CO \cdot ONH_4$, and contains about 31 p.c. of ammonia and 56 p.c. of carbon dioxide. It is usually prepared by subliming a mixture of about 1 part of ammonium sulphate with 1·5 to 2 parts of chalk in retorts, the evolved gases being passed into leaden chambers, where the carbonate is deposited as crusts on the walls, the exit gases being washed with water or sulphuric acid to recover the uncondensed ammonia. Lunge recommends the passing of an additional quantity of carbon dioxide through the chambers to effect a more complete recovery of the ammonia. As soon as the crust has attained a sufficient thickness it is detached, and is usually purified by resublimation. In Kunheim's process, the carbonate is prepared by passing ammonia obtained by the distillation of gas liquor direct into chambers, where it mixes with carbon dioxide and deposits the carbonate as a crust. (*See also* Bueb, Eng. Pat. 9177, 1910.)

The commercial product forms crystalline crusts, smelling strongly of ammonia, which is partially evolved on exposure to the air, the mass effforescing and leaving a powder consisting of ammonium bicarbonate. It is employed in wool-scouring, dyeing, and as a constituent of baking powders.

Ammonium Nitrate.—This salt is produced to a considerable extent for use in the explosive industry and in the preparation of nitrous oxide. It may be obtained by neutralising caustic ammonia with nitric acid, and evaporating and crystallising the solution if necessary, or by heating a mixture of ammonium sulphate and sodium nitrate in equivalent proportions, either alone or in solution. When the solution is concentrated, sodium sulphate separates out first for the most part, but the ammonium nitrate obtained simply by further evaporation is far from pure. According to Wedekind and Co. (Eng. Pat. 19465, 1906); a pure salt may be produced by a modified system of evaporation, of which the following example is given. A mixture of 400 parts of ammonium sulphate and 720 parts of sodium nitrate (40 p.c. excess) is dissolved in 900 parts of water, and the bulk of the sodium sulphate formed separated by evaporation. The filtered liquor is further concentrated till a sample on cooling to 70° deposits ammonium nitrate; the whole solution is then cooled to slightly above 70°, and after removal of the copious deposit of crystals of sodium nitrate and sulphate, the mother liquor is mixed with sufficient water to prevent the separation of sodium salts at 15°, 14 parts of water per 100 of mother liquor being sufficient with the above quantities. On then cooling to 15°, about 40 p.c. of the ammonium nitrate separates in the pure state. The mother liquor from these crystals, and the sodium nitrate previously separated, are employed in working up a further amount of ammonium sulphate.

The nitrate is also manufactured from the calcium nitrate now commercially prepared from the oxides of nitrogen obtained by the oxidation of atmospheric nitrogen, by heating it with a solution of rather less than an equivalent quantity of ammonium sulphate. Under proper conditions the reaction is said to be almost quantitative, the calcium sulphate separating in a readily removable form (Wedekind & Co. Eng. Pat. 20907, 1909). Attempts to obtain the nitrate from the calcium salt by the action of ammonia and carbon dioxide have not hitherto proved successful, owing to the formation of double salts.

Ammonium phosphate. Monammonium phosphate $(NH_4)H_2PO_4$, and diammonium phosphate $(NH_4)_2HPO_4$ have become commercial products by the process of Lagrange, which starts from commercial calcium superphosphate. This is lixiviated by water and steam, and a solution of 42°Tw. is obtained, together with a residue of calcium sulphate. Some of the latter remains in the solution, and is removed by carefully adding barium carbonate. The filtrate is neutralised by ammonia in slight excess, whereby all the lime is precipitated as basic phosphate, which is washed and used over again for the manufacture of superphosphate. The filtered solution, marking 32°Tw., contains monammonium phosphate, and can be worked for this or for diammonium phosphate. The latter is obtained by gradually mixing the above solution with *liquor ammoniæ* of sp.gr. 0·92, in the proportion of 1½ equivalents of NH_3 to 1 of $(NH_4)H_2(PO_4)$. The diammonium phosphate at once separates out as a crystalline mass, which, after cooling, is submitted to hydraulic pressure. The operation is carried out in a closed vessel, to prevent the escape of ammonia. The mother liquor is employed for the manufacture of ammonia. The diammonium phosphate is principally used in Lagrange's sugar-refining process.

Ammonium thiocyanate is manufactured in considerable quantity in the crude state, but the product is for the most part simply employed as an intermediate product in the manufacture of cyanides. It occurs, as has been mentioned, in considerable amount in gas-liquor, and also in spent oxide, from which it may be extracted by water, but in both cases it is mixed with so many other impurities that its recovery is not remunerative; it may, however, be easily isolated as cuprous thiocyanate by precipitation

with copper sulphate and sulphurous acid. It is prepared synthetically from carbon disulphide by absorbing the latter in ammonia in presence of bases such as lime (Albright and Hood, Eng. Pat. 14154, 1894), the ammonium thiocarbonate first produced undergoing conversion into thiocyanate. A concentrated solution of ammonium thiocyanate is now prepared in a number of gas works, according to the British Cyanide Co.'s process (Eng. Pat. 13653, 1901), by passing the crude gas containing ammonia and hydrocyanic acid through a washer containing water and fed with powdered sulphur, the ammonium polysulphide first formed combining with the hydrocyanic acid to form thiocyanate, solutions of 30–50 p.c. strength being readily obtained, which only contain small amounts of other non-volatile ammonium salts.

The pure salt is used in dyeing and calico-printing, and may be obtained from the crude product by first converting it into the barium salt with baryta-water ; or the barium salt may be produced by the action of barium sulphide on cuprous thiocyanate. After purification by recrystallisation, the barium salt is exactly precipitated with ammonium sulphate, and the solution evaporated and crystallised. The white deliquescent salt has frequently a reddish colour, due to the formation of the red ferric thiocyanate, from traces of iron present.

Ammonium persulphate. This salt is now produced on the commercial scale by the electrolysis of ammonium sulphate, and is employed for photographic purposes and as an oxidising agent. The commercial product usually contains small quantities of lead derived from the electrodes used in its manufacture.

H. G. C.

AMMONIACUM, AFRICAN, *v.* GUM RESINS.
AMMONIACUM, GUM, *v.* GUM RESINS.
AMMONIACUM, PERSIAN, *v.* GUM RESINS.
AMMONITE *v.* EXPLOSIVES.
AMMONIUM MELEQUETA *v.* COCCULUS INDICUS.

AMRAD-GUM. This gum forms white, yellow, and brown lumps of a sweetish taste and resinous smell. An aqueous solution (1 : 2) is viscid and strongly adhesive. It also gives with oil excellent emulsions, which keep very well. The dry substance contains 5·61 p.c. of ash, consisting of carbonic acid, lime, iron, magnesia, traces of phosphoric acid and silica. Has been recommended as a substitute for gum arabic. It was brought into the market some years ago, and comes from the Abyssinian highlands ; is probably obtained from *Acacia etbaica* (Schweinfurth). (H. Unger and Kempf. Pharm. Zeit. 33, 218 ; J. Soc. Chem. Ind. vii. 446.)

AMYGDALASE, AMYGDALIN *v.* GLUCOSIDES.

AMYGDONITRILE GLUCOSIDE *v.* GLUCOSIDES.

AMYGDOPHENIN *v.* SYNTHETIC DRUGS.

AMYL ACETATE *v.* ACETIC ACID.

AMYL ALCOHOL $C_5H_{12}O$. The ordinary amyl alcohol (fusel oil), fermentation amyl alcohol, or *iso*amyl alcohol Cl-hydroxy-3-methyl butane) is one of the eight alcohols of the formula $C_5H_{12}O$ theoretically possible, and is the chief constituent of the fusel oil or 'last runnings' obtained in the rectification of alcohol, particularly of the alcohol made by the fermentation of potatoes. Amyl alcohol is a constituent of the product obtained when ordinary alcohol is formed by fermentation. The alcohol is got from the 'last runnings' by shaking the crude product with hot milk of time, decanting, drying over calcium chloride, and rectifying at a temperature of 132°. Pure amyl alcohol is obtained by preparing potassium amyl sulphate, purifying this by solution in alcohol and precipitation with ether, and subsequently decomposing by heating for five hours with 10 p.c. sulphuric acid.

Properties.—Amyl alcohol is a colourless liquid with a peculiar cough-exciting odour and a burning taste ; it burns with a white smoky flame ; b.p. 131·6° (corr.) and sp.gr. 0·8248 at 0° ; 0·8113 at 18·7° (Kopp, Annalen, 94, 289); b.p. 128·9°–129·2° at 740·9 mm., and sp.gr. 0·8104 at 20°/4° (Brühl, Annalen, 203, 23) ; b.p. 130·5°–131° at 759·2 mm. (Schiff, Annalen, 220, 102). It is soluble in ethyl alcohol or ether, but is soluble in water only to the extent of 1 in 39 at 16·5° (Wittstein, J. 1862, 408), and 1 in 50 at 13°–14°, and the solution becomes milky at 50° (Balbiano, Ber. 1876, 1437). Amyl alcohol dissolves in all proportions in acetic acid diluted with an equal bulk of water (Berthelot and St. Gilles, J. 1862, 408). When oxidised with platinum black, ordinary valeric (*iso*valeric) acid is formed, whilst distillation with either manganese dioxide or potassium dichromate and sulphuric acid converts it into *iso*valer-aldehyde and *iso*valeric acid. Sulphuric acid dissolves it in the cold, forming amyl-sulphuric acid, which, on heating, decomposes into amylene and its polymerides diamylene and tetramylene ; these hydrocarbons, together with hexylene and the corresponding paraffins, are also obtained when amyl alcohol is distilled with zinc chloride (Wurtz, Annalen, 128, 316) : it is probable, however, that the latter owe their formation to impurities in the alcohol. The action of chlorine has been studied by Barth (Annalen, 119, 216), and that of bleaching powder by Goldberg (J. pr. Chem. [2] 24, 116). The bromide (Cahours, Annalen, 30, 298; Balbiano, J. 1876, 348), chloride (Cahours, Annalen, 37, 164 ; Balard, Annalen, 52, 312 ; Balbiano, *l.c.*), and iodide (Cahours, Annalen, 30, 297) have been prepared by the action of the corresponding phosphorus compounds. Commercial amyl alcohol is generally lævorotatory ; the degree of rotation, however, is not constant, but varies in different specimens, and the variation has been shown by Pasteur (Annalen, 96, 255) to be due to the fact that ordinary amyl alcohol is a mixture, in varying proportions, of two isomerides, one of which is optically inactive, and the other lævorotatory. When ordinary amyl alcohol is treated with sulphuric acid and the resulting amyl sulphuric acids converted into barium salts by neutralisation with barium carbonate, a separation of the two isomeric alcohols can be effected, inasmuch as the barium salt of the optically active alcohol is 2½ times more soluble in water than the corresponding salt of the optically inactive modification. (For an examination of the properties and physical constants of commercial amyl alcohol, *see* Richmond and O'Shaughnessy, J. Soc. Chem. Ind. 1899, 107.) Marckwald and McKenzie have reviewed the previous work of

Ley, Le Bel, Bakhoren, and Chapman. They have succeeded in dividing the commercial alcohol into its constituents by fractional crystallisation of their nitrophthalic esters, and find that active amyl alcohol has $[a]_D$ $-5·90°$ at 20°. The other constituent is *iso*butyl carbinol (Ber. 1901, 485, 479; 1909, 1583).

Amyl alcohol has been used as a solvent for nitrocellulose in the manufacture of celluloid, as have also its chlorination products Liebert has utilised amyl nitrate (D. R. P. 51022) by adding it to nitroglycerine in order to diminish its sensitiveness to cold and concussion.

In addition to the optically active and inactive modifications obtained from ordinary amyl alcohol, the following isomeric alcohols have been prepared :—*Normal amyl alcohol* (Lieben and Rossi, Annalen, 159, 70 ; Schorlemmer, Annalen, 161, 268); *methylpropyl carbinol* (Schorlemmer, *l.c.* ; Saytzew and Wagner, Annalen, 175, 351 ; 179, 313 ; Markownikow, J. 1883, 861); *methylisopropyl carbinol* (Wyschnegradsky, *l.c.* ; Münch, Annalen, 180, 339 ; Winagradow, Annalen, 191, 125); *diethyl carbinol* (Saytzew and Wagner, *l.c.*); *dimethylethyl carbinol* (Wurtz, Annalen, 125, 114 ; 127, 236 ; 129, 365 ; Berthelot, Annalen, 127, 69 ; Flavitzky, Annalen, 179, 348 ; Wyschnegradsky, *l.c.* ; Osipoff, Ber. 1875, 1240).

AMYL NITRITES $C_5H_{11}NO_2$. **Commercial amyl nitrite** is a mixture of the nitrites of *iso*butyl carbinol and active amyl alcohol

$$(CH_3)_2CH·CH_2·CH_2·NO_2 + CH_3(C_2H_5)CH·CH_2·NO_2$$
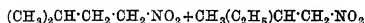
It may also contain *iso*butyl nitrite, and always contains some unaltered amyl alcohol. Curtmann (J. Soc. Chem. Ind. 1893, 372) gives examples of specimens containing from 33 p.c. to 93 p.c. of amyl nitrite. It is prepared by passing nitrous fumes into amyl alcohol (Balard, Ann. Chim. Phys. [3] 12, 318 ; Williams and Smith, Pharm. J. 1886, 499); by distilling together the theoretical quantities of amyl alcohol and potassium nitrite with excess of dilute sulphuric acid ; or by passing nitrosyl chloride into a mixture of equimolecular proportions of dry pyridine and amyl alcohol (Bouveault and Wahl, Compt. rend. 136, 1563). The last is a general method for the preparation of nitrous esters, and gives a yield of 80 p.c. in the case of amyl nitrite. The commercial article is a yellow liquid with characteristic odour, which should boil between 97° and 99°, and have a sp.gr. 0·870 to 0·880. It is of value as a stimulant in angina pectoris and similar affections.

Normal amyl nitrite $CH_3·(CH_2)_3·CH_2NO_2$ is a pale-yellow liquid, boiling at 104° ; sp.gr. 0·8528 at 20°. The nitrite group is readily removed by dilute potash (Marcel Pexsters, Chem. Zentr. 1907, i. 1398).

Isobutyl carbinol nitrite

$$\begin{matrix}CH_3\\CH_3\end{matrix}{>}CH·CH_2·CH_2·NO_2$$
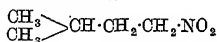
from pure *iso*butyl carbinol, boils at 97°, and has sp.gr. 0·880 (Dunstan and Williams, Pharm. J. 1889, 487).

Tertiary amyl nitrite $(CH_3)_2(C_2H_5)C·NO_2$ (Bertoni's amylonitrous ether) has been used as a substitute for ordinary amyl nitrite, its action being stronger in degree and more lasting. It is a yellow liquid with weak camphoraceous odour,

tasting like peppermint. It boils at 93° (J. Soc. Chem. Ind. 1889, 1003).

AMYLACETIC ACID (Active) *v.* HEPTOIC ACIDS.

iso-**AMYLACETIC ACID** *v.* HEPTOIC ACIDS.

a- and *β*-**AMYLANS** $n(C_6H_{10}O_5)$?

After first extracting cereals with strong alcohol, the aqueous extract contains gummy lævorotatory colloidal carbohydrates, which are precipitated by strong alcohol. The product so obtained from barley is a mixture, part being soluble in cold water. The insoluble crumbly residue, amounting to 2 p.c. of the barley, is *a*-amylan. It has $[a]_D$ $-21·6$, and does not reduce Fehling's solution ; it is gelatinised in hot water, and yields viscous solutions even at 1–2 p.c. concentration. O'Sullivan (Chem. Soc. Trans. 1882, 41, 24) found it to be present in barley, oats, wheat, and rye, especially in the two first named. The soluble product *β*-amylan has $[a]_D$ $-65°$; it amounts to 0·3 p.c., and is very similar to *a*-amylan in properties.

O'Sullivan obtained from *β*-amylan, by fractional precipitation with alcohol or on boiling with milk of lime, a similar substance $[a]_D$ $-129·7°$. This he regarded as a decomposition product, but this is probably not the case. O'Sullivan states that the amylans yield glucose alone on hydrolysis. Lintner and Düll (Zeit. angew. Chem. 1891, 538) obtained galactose and xylose from barley gum. Wroblewski (Ber. 1893, 30, 2289) obtained arabinose. Lindet (Berlin Congress, 1903, 3, 498) isolated a dextrorotatory gum from barley, in addition to a lævo-rotatory gum.

Contrary to O'Sullivan's statement that diastase is without action on amylan, Horace Brown (Trans. Guinness Research Laboratory, 1906, 317, where there is a full account of amylan) finds that when barley gum is steeped in malt extract it swells up and undergoes gradual liquefaction and solution, and in a few days its colloidal nature is lost. This is one of the most significant changes which mark the conversion of barley into malt.

To prepare ' amylans ' in quantity, Brown boils the finely divided grain with water, treats with malt extract at 50°–55° for an hour to liquefy the starch, boils again, and filters. The filtrate is concentrated in vacuum to sp.gr. 1·060, and three volumes 80 p.c. alcohol (by volume) added gradually. The crude amylans are precipitated in large white flocks free from dextrin and have no cupric reducing power. Corrected for ash and nitrogen they amount on a number of dry barleys to about 9·6 p.c., and have $[a]_D + 62°$ to $+73°$. This amount practically accounts for the whole of the missing constituents of the soluble portion of barley after hydrolysis with malt extract.

On hydrolysis about 60 p.c. of glucose is formed, together with arabinose, xylose, and an unknown substance of low angle and reducing power.

The above dextrorotatory amylan represents everything insoluble in 62 p.c. alcohol. By a variation of the method of preparation a carbohydrate $[a]_D - 100·34°$, corresponding to Wroblewski's araban, was obtained.

It is obvious that the ' amylans ' require further investigation. According to O'Sullivan, it is probably owing to the presence of amylan

that unmalted barley cannot be satisfactorily employed in the preparation of beer. Malted grain does not contain it. Distillers using raw grain (oats and barley) have at times much difficulty in separating the wort (solution of sugars, &c.) from the grains (undissolved portion of the grain employed) in consequence of the presence of amylan in quantity, the barleys and oats of some seasons containing much more of it than at other times.   E. F. A.

AMYLASE *v.* DIASTASE; *also* ENZYMES.

AMYLENE C_5H_{10}. Eight isomeric amylenes are theoretically possible, and all have been prepared. These hydrocarbons have been chiefly studied by Flavitzky (Annalen, 179, 340), Wyschnegradsky (Annalen, 190, 336), and by Kondakoff (J. Russ. Phys. Chem. Soc. 24, 381), and can be obtained by the action of alcoholic potash on the various amyl iodides; or by the action of dehydrating agents such as sulphuric acid or zinc chloride on amyl alcohol. They can often be converted into one another by the action of hydriodic acid and the subsequent removal of the latter, thus:

$Me_2CH \cdot CH : CH_2 \dotplus HI$

$\rightarrow Me_2CH \cdot CHIMe \overset{KOH}{\underset{+alcohol}{\rightarrow}} Me_2C : CHMe$.
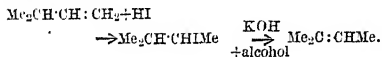
The amylene ordinarily met with is trimethylethylene, and is chiefly obtained by the dehydrating action of zinc chloride on fermentation amyl alcohol.

Preparation.—To prepare amylene, fermentation amyl alcohol (1 part) is shaken with coarsely powdered zinc chloride ($1\frac{1}{2}$ parts), allowed to remain for twenty-four hours, and then distilled. The product consists of a complex mixture of paraffins from C_5H_{12} to $C_{10}H_{22}$ with olefines from C_5H_{10} to $C_{10}H_{20}$ (Wurtz, J. 1863, 507). These can be isolated by fractional distillation (Wurtz), but according to Eltekow (J. Russ. Chem. Soc. 14, 379), amylene is most readily obtained if the product is well cooled, and shaken with dilute sulphuric acid (2 vols. of acid to 1 vol. of water), the acid layer separated, diluted with water, and distilled; the distillate consists of amylene (trimethylethylene) and tertiary amyl alcohol, and the latter, on distillation with sulphuric acid (1 : 1), yields pure trimethylethylene. Pure trimethylethylene can be prepared by heating tertiary amyl iodide Me_2CIEt with alcoholic potash (J. Russ. Phys. Chem. Soc. 17, 294). It can also be formed by dropping tertiary amyl alcohol on to oxalic acid (D. R. P. 66866).

Other methods for obtaining ordinary amylene have been described by Balard (Ann. Chim. Phys. [3] 12, 320); Bauer (J. 1861, 659), and Linnemann (Annalen, 143, 350); Kondakoff (*l.c.*); Ipatieff (J. Russ. Phys. Chem. Soc. 30, 292); Tornöe (Ber. 21, 1282); Blaise and Courlot (Bull. Soc. chim. 35, 582).

Properties.—Amylene is a colourless liquid, b.p. 36°–38° and sp.gr. 0·6783 at 0° (Le Bel, Bull. Soc. chim. 25, 547); b.p. 36·8° at 752·7 mm. (Schiff, Annalen, 223, 65). It combines directly with a large number of substances: with nitric peroxide (Guthrie, Chem. Soc. Trans. 13. 129; Wallach, Annalen, 241, 291; 248, 161; Miller, Chem. Soc. Proc. 3, 108; Demganoff, Chem. Zentr. 1899, i. 1064); sulphur chloride and chlorine (Guthrie, Chem. Soc. Trans. 12, 112;

13, 45, 129; 14, 136; Kondakoff, J. Russ. Phys. Chem. Soc. 20, 141; 24, 381; Ber. 24, 929; Hell and Wildermann, *ibid.* 216); with bromine (Wurtz, Ann. Chim. Phys. [3] 55, 458; Hell and Wildermann, *l.c.*; Kondakoff, *l.c.*), and, when cautiously mixed with well-cooled sulphuric acid, sp.gr. 1·67 (2 vols. H_2SO_4 to 1 vol. water), in a freezing mixture, is converted into dimethylethyl carbinol, b.p. 101·6°–102°/762·2 mm., which has valuable hypnotic properties (J. Soc. Chem. Ind. 8, 1002; 9, 650, 889), and can be obtained, after neutralisation with sodium hydroxide; on distillation (Flavitzky, 175, 157) with sulphuric acid, sp.gr. 1·545 (2 pts. by weight H_2SO_4 to 1 pt. water), methyl*iso*propyl carbinol is obtained (Osipoff, Ber. 8, 542, 1240). Amylene forms compounds with metallic salts (Denigès, Compt. rend. 126, 1146; Kondakoff, J. Russ. Phys. Chem. Soc. 25, 35). When heated to high temperatures, benzene, naphthalene, acetylene, methane, carbon, and hydrogen are produced, the products depending on the temperature (Haber and Oechelhäuser (Chem. Zentr. 1897, i. 225). The action of nitrosyl chloride on amylene has been studied by Tilden and Sudborough (Chem. Soc. Trans. 1893, 482).

In addition to ordinary amylene, the following isomerides have been obtained :—*Normal amylene*, b.p. 39°–40° (Wurtz, Annalen, 123, 205 ; 127, 55 ; 148, 131 ; Zeidler, Annalen, 197, 253 ; Kondakoff, J. Russ. Phys. Chem. Soc. 24, 113 ; Flavitzky and Wyschnegradsky, *l.c.*) ; *isopropylethylene*, b.p. 21·1°–21·3° (Flavitzky and Wyschnegradsky, *l.c.* ; Kondakoff, *l.c.* ; Ipatieff, *l.c.*) ; *symmetrical methylethylethylene*, b.p. 36° at 740·8 mm. (Wagner and Saytzew, Annalen, 175, 373 ; 179, 302 ; Kondakoff, *l.c.* ; Lissier, Bull. Soc. chim. 9, (3) 100) ; and *unsymmetrical methylethylethylene*, b.p. 31°–32°, sp.gr. 0·67 at 0° (Wyschnegradsky, *l.c.* ; Le Bel, Bull. Soc. chim. 25, 546 ; Kondakoff, *l.c.* 25, 354) ; *Methyltetramethylene*, b.p. 39°–42° (Coleman and Perkin, Chem. Soc. Trans. 1888, 201) ; *pentamethylene*, b.p. 35° (Gustavson and Demganoff, J. Russ. Phys. Chem. Soc. 21, 344 ; Markownikoff, Ber. 30, 975 ; Young, Chem. Soc. Trans. 1898, 906 ; Wislicenus and Hanschel, Annalen, 275, 327) ; and *dimethyltrimethylene* (Gustavson and Popper, J. pr. Chem. 166, 458).

The action of hydrogen iodide on the amylenes has been investigated by Saytzew (Annalen, 179, 126) ; whilst Zeidler (Annalen, 186, 245) has examined the products obtained when various amylenes are oxidised with potassium permanganate in acid, neutral and alkaline solution, with chromic acid, and with potassium dichromate and sulphuric acid. The halogen derivatives of the various amylenes have been investigated (Lip— Ber. 22, 2572 ; Hell and Wildermann, 23, 3510 ; Ipatieff, J. pr. Chem. 161, 257 ; Chem. Zentr. 1898, ii. 472 ; Brochet, Ann. Chim. Phys. 1897, 10, 381 ; Wassileef, Chem. Zentr. 1899, i. 775 ; Froebe and Hochstetter, Monatsh. 23, 1075 ; Kukuritschkin, J. Russ. Phys. Chem. Soc. 35, 873 ; Schmidt and Leipprand, Ber. 37, 532 ; Hamonet, Compt. rend. 138, 1609). Also the action of oxalic acid on various amylenes (Miklosheffsky, J. Russ. Phys. Chem. Soc. 22, 495), the nitrolamines (Wallach and Wohl, Annalen, 262, 324), and the nitrosites and nitrosates (Ipatieff, Chem. Zentr. 1899, ii. 178 ; Schmidt, Ber. 35, 2323, 2336, 3737 ; Hantzsch,

2978, 4120 ; Schmidt and Austin, Ber. 36, 1768).

The following polymerides of amylene have also been obtained, and can be prepared by heating ordinary amyl alcohol or amylene with zinc chloride :—*Diamylene* $C_{10}H_{20}$, b.p. 157°–157·5°/759 mm. (Balard, Annalen, 52, 316 ; Schneider, Annalen, 157, 207 ; Bauer, Jahresbericht. 1861, 660 ; Kondakoff, J. pr. Chem. 162, 442 ; Gasselin, Ann. Chim. Phys. 1894, 3, 5) ; *triamylene* $C_{15}H_{30}$ (Bauer, *l.c.* : Gasselin, *l.c.*) ; and *tetramylene* $C_{20}H_{40}$ (Bauer, *l.c.*). Also derivatives of diamylene (Schindelmeister, Chem. Zentr. 1896, ii. 354).

AMYLOCARBOL. Trade name for a disinfectant, said to consist of carbolic acid 9 pts., amyl alcohol 160 pts., green soap 150 pts., water 690 pts.

AMYLOCOGULASE *v. Enzymes*, art. FERMENTATION.

AMYLOFORM. An antiseptic prepared by the action of formic aldehyde upon starch (Claassen, Pharm. Zeit. 41, 625) (*v.* SYNTHETIC DRUGS).

AMYRIN *v.* OLEO-RESINS.

ANACAHUITA. A wood of unknown botanical origin imported from Mexico ; its preparations are said to be useful in pulmonary disorders. The wood contains a volatile oil, an iron-greening tannin, gallic acid, a yellowish resin, sugar, a tasteless volatile body crystallising in warty masses, and a bitter substance crystallising in white needles (J. 1861, 771).

ANACARDIUM NUT (Cashew Nut, Kajoo) is the fruit of *Anacardium occidentale* (Linn.), a tree indigenous to Brazil, Central America, and the West Indies. It has been transplanted to, and become naturalised in, many parts of India. The fruit rests on a fleshy edible peduncle, from which a spirit is distilled in Mozambique and in Western India. The nut is edible after it has been roasted to expel the cardol which it contains ; the cardol thus obtained is used at Goa for tarring boats, and as a preservative of woodwork (Dymock, Pharm. J. [3] 7, 730). In addition to cardol, the nuts contain anacardic acid, and an oily matter which, by exposure to the air, assumes a fine black colour, permanent against acids, alkalis, chlorine, and hydrocyanic acid. It has been recommended as a marking ink, and is used for giving a black colour to candles (Böttger, Dingl. poly. J. 205, 490). From the stem of the plant a gum exudes which is said to be used by book-binders in South America.

The kernels contain 47·2 p.c. of a fatty oil, having the following characteristics :—Saponification value, 187 ; iodine value, 77–83·6 ; refraction in Zeiss' butyro-refractometer at 25°, 58·1–58·8 (Theopold, Pharm. Zeit. 1909, 1057).

J. L.

ANÆSTHETICS. There are three principal types of anæsthesia, or loss of sensation sufficient to allow of surgical operations without pain. In *local* anæsthesia the actual tissues to be lacerated are infiltrated with some substance which paralyses the endings of the nerves that convey painful sensations. In *general* anæsthesia, total insensibility and loss of muscular power are produced by the action of drugs on the brain, carried there in the circulation ; extensive operations on any part of the body can then be done. In *spinal* anæsthesia, the whole of the nerves supplying large sections of the body are paralysed at their exit from the spinal cord by applying to the latter a drug which is injected into the vertebral canal. Thus spinal anæsthesia resembles general anæsthesia inasmuch as it causes loss of sensation and muscular power together over a wide region, and local anæsthesia in that consciousness is not lost and the anæsthetic is not diffused in the circulation.

Local anæsthetics. Very little is known of the action of these on the tissues with which they come in contact. They are all protoplasmic poisons which have a special preferential action upon nervous structures. Those in common use are : cocaine, stovaine, novocain, tropacocaine, β-eucaine, alypin, β-eucaine lactate, nirvanine, holocaine hydrochloride, acoine, orthoform, anæsthesine. Braun has formulated postulates for appraising local anæsthetics. Omitting one which has not secured general assent, they are :

(1) Low toxicity in proportion to local anæsthetising power.

(2) Solubility in water to 2 p.c. at least ; and stability of the solution, which should keep without deteriorating and be capable of sterilisation by boiling.

(3) Non-irritability to the tissues, and freedom from after-effects when absorbed into the circulation.

(4) Compatibility with adrenalin.

Acoine, holocaine hydrochloride, anæsthesine, and orthoform are more or less insoluble. β-eucaine is about on the 2 p.c. border line. The others are freely soluble and will keep without deteriorating. Cocaine solutions cannot be boiled, but stovaine, novocain, β-eucaine lactate, tropacocaine, alypin, and nirvanine can be thus sterilised, at 115° if necessary.

The most powerful anæsthetic action is that of stovaine. Next are cocaine, novocain, tropacocaine, alypin, and β-eucaine lactate, which are all about equal. The others have inferior actions in this respect. Experiments on mice and rabbits have resulted in the following table of relative toxicity, cocaine being taken as the unit [1] :—

Alypin, 1·25	Stovaine, 0·625
Cocaine, 1·00	Novocain, 0·490
Nirvanine, 0·714	β-eucaine lactate, 0·414

The irritant action of stovaine, tropacocaine, and β-eucaine lactate is greater than that of cocaine ; that of novocain is less. All these five are compatible with adrenalin if the solutions are fresh mixed for each case. They are extensively employed ; but novocain is evidently the best yet discovered for routine use.

Local anæsthetics are used dissolved in water or in normal saline solution. It is not essential that they should be injected subcutaneously ; where the surface tissues are delicate, as on the eye, larynx, tongue, tonsils, simple contact with a local anæsthetic in solution or in fine powder will destroy sensation sufficiently for many surgical procedures. But elsewhere the solution is injected with a hypodermic syringe into the tissues which are to be rendered anæsthetic. If adrenalin be mixed with the anæsthetic solution, contraction of all the minute blood-vessels in the locality takes place.

[1] Le Brocq, Pharm. J. 1909, 674.

Thus the drug is retained longer in the tissues about the site of injection, instead of being rapidly dissipated in the blood-stream. Consequently a more intense and lasting, because more strictly local, action occurs.

Local anæsthesia can also be obtained by freezing the superficial tissues. A fine jet of ether or ethyl chloride is directed on to the desired portion of the skin, and when the latter is frozen a cut can be made, as for a whitlow, boil, or other small abscess, without causing pain.

Spinal anæsthetics. Some of the same drugs which cause local anæsthesia are available for injection into the cerebro-spinal fluid with which the spinal cord is surrounded in the vertebral canal. Stovaine and novocain are most used in Britain, but tropacocaine also is popular in Europe. The method was introduced by Bier in Germany in 1899, and since 1907 has been very extensively tried all over the world. The balance of opinion is that for ordinary cases spinal anæsthesia is too dangerous to replace general anæsthesia ; but that for certain cases where the latter entails especial risks, it is of undoubted utility. Barker [1] and McGavin,[2] who are the most prominent advocates of spinal anæsthesia in England, use a solution of stovaine in 5 p.c. glucose ; 4 to 7 centigrammes of stovaine is the dose for an adult. Ryall, following Jonnesco of Bucharest, adds half to one milligramme of strychnine to 4 to 10 centigrammes of novocain.[3] Strychnine is also used with stovaine, and with tropacocaine ; the object is to prevent the anæsthetic from causing death if it should by any chance reach the respiratory centre near the upper end of the spinal cord. Bier has used morphia with scopolamine (hyoscine) as a preliminary, injected hypodermically ; but he seems now to be convinced that the method which he originated is too risky to replace general anæsthesia.[4]

General anæsthetics. There are many substances which diminish or abolish the perception of pain ; but only a few of these are freely used as general anæsthetics. The conditions which must be fulfilled to obtain admission to the list are [5]:

(1) To produce absolute insensibility to pain without causing any great discomfort during induction.

(2) To produce loss of all voluntary and many reflex movements.

(3) To be capable of being readily introduced into the system, and rapidly eliminated, after the completion of the operation, without injury to the patient.

(4) To act in a regular and constant way, so that the effects can be controlled by the administrator.

The general anæsthetics in use in Great Britain are four in number : nitrous oxide, ethyl chloride, ether, chloroform. Ethyl bromide, ethidene dichloride (dichlorethane), bichloride of methylene, and amylene (pental) are obsolete. In

¹ British Medical Journal, 1908, ii. 453 (and other papers).
² Practitioner, August, 1909; British Medical Journal, Sept. 17, 1910.
³ Clinical Journal, July 17, 1909.
⁴ Deutsch. Zeitschr. f. Chirurgerie, xcv. 373.
⁵ R. W. Collum, The Practice of Anæsthetics, 1909, 14.

America and on the Continent anæsthol, somnoform, and narcotile are also employed. Anæsthol is a mixture of chloroform, ether, and ethyl chloride, in molecular proportions ; somnoform is ethyl chloride 60 parts, methyl chloride 35 parts, ethyl bromide 5 parts ; narcotile has been stated to be a compound, but analysis has shown it to be a mixture of methyl chloride, ethyl chloride, and ether. Mixtures of ether and chloroform in various proportions are in common use everywhere. Morphine, chloral, cannabis indica, and many other drugs have analgesic and anæsthetic properties ; some of them, morphine especially, are used to assist the action of the volatile anæsthetics.

The effects of a general anæsthetic are produced by the circulation in the blood of the drug employed. When it reaches the brain the phenomena of anæsthesia are exhibited : at first slightly, then with increasing doses more and more intensely, until with a sufficient quantity death results. The phenomena of general anæsthesia are the same whether absorption takes place through the lungs, rectum, skin, or gastro-intestinal tract. Thus alcohol has a marked anæsthetic effect, familiar in the indifference of a drunken man to injury.

The easiest way of introducing into the blood any substance which is a gas or a volatile liquid is by means of the lungs. The blood thus charged with an anæsthetic is rapidly delivered to the nervous centres, in which the essential changes of general anæsthesia take place. The absorption of vapours in the lungs varies with numerous factors : barometric pressure, temperature of the vapour and of the blood, rate of respiration, and rate of blood-flow through the pulmonary system. But the process is also something more than simple solution by diffusion of gases through a thin membrane ; there is at least an element which depends on the fact that the tissues concerned are living.

The lungs are also the chief, but not the only, medium for the elimination of inhaled anæsthetics. These are but little decomposed during their tour of the circulation, and the greater part is discharged unchanged after the administration is suspended. What change they undergo in the blood is very uncertain. Chloroform, which has hitherto received more attention in this respect than the others, is recoverable from the blood in fatal cases of chloroform anæsthesia, but it is believed that most of it circulates in the red corpuscles of the blood in combination with the lecithin and cholesterin which they contain.[1] Glycuronic acid not uncommonly appears in the urine after chloroform anæsthesia. Nitrogen and sulphur are also excreted in the urine in greater quantity, indicating a greater destruction of proteid ; and the increase of chlorides is held to show that some chloroform is decomposed in the body. The affinity of cholesterin and lecithin for chloroform, chloral, ether, sulphonal, tetronal, trional, and chloralamide has been suggested as the explanation for the selective action of these narcotics on the central nervous system, which contains a larger proportion of cholesterin and lecithin than do the other organs. With regard to ether, Turnbull states that etherisation

¹ Hale White, Materia Medica, 11th ed. 1909, 280.

produces a marked diminution of the hæmoglobin of the blood [1]; and Reicher finds three times the normal quantity of fat present in the blood, together with an increased amount of acetone, due to the disintegration of fat and albuminoid bodies.[2] The chemical composition of the blood is often much modified during anæsthesia, because the air supply to the lungs is frequently curtailed to a greater or less extent, and the elimination of CO_2 hindered. The proportions of O and CO_2 in the circulating blood may thus be altered at the expense of the former, and an asphyxial element added to the narcotic effect of the anæsthetic. Some authorities believe that deprivation of oxygen is the method by which all anæsthetics produce their action on the nervous tissues.[3]

The chemical changes which may be assumed to take place in the brain during anæsthesia are unknown, as indeed are those of natural sleep. It has been suggested that unstable compounds are formed between the anæsthetic and the protoplasm of the nerve cells, and some observers describe changes recognisable microscopically in those cells as a result of anæsthesia. Professor Hans Meyer holds that there is a loose physico-chemical combination with the lipoids of the cell. This causes inhibition of the normal metabolism until the loose reversible combination breaks up. A rare sequel of chloroform anæsthesia is known as delayed chloroform poisoning. The symptoms of this condition, which is sometimes fatal, arise about eighteen to seventy-two hours after the anæsthesia. They are attributed to 'acidosis,' that is to diminished alkalinity of the blood due to the presence of acetone and aceto-acetic acid, which can be detected in the urine and the breath. For the developed condition sodium bicarbonate in large doses is employed; as a preventive measure feeding on glucose for a day or two before operation is found to answer best.[4] Very rarely indeed this acidosis has followed the administration of ether.

Nitrous oxide (Laughing gas).—The inhalation of from three or four to twenty or thirty gallons of this gas without any air produces anæsthesia. If the administration is then suspended, insensibility lasts on an average about thirty to forty-five seconds, during which time minor operations such as the extraction of teeth can be undertaken. A marked asphyxial element is nearly always present, owing to the replacement of oxygen by N_2O. If air be admitted for brief periods between successive doses of gas, anæsthesia can be maintained without great difficulty for several minutes. By delivering nitrous oxide mixed with pure oxygen for inhalation, anæsthesia can be prolonged for any desired period. The proportions of the two gases are varied to meet the requirements of individual cases, but roughly the mixture must contain about 80 p.c. by volume of N_2O. The previous injection of narcotics such as morphine, with atropine, facilitates the induction of anæsthesia. This method is well suited for operations on the limbs, but for abdominal operations it is difficult to get the complete

muscular relaxation necessary. Nitrous oxide gas is the safest known general anæsthetic, and recovery takes place very rapidly (two or three minutes) without unpleasant after-effects.

Ethyl chloride.—The vapour of 3 to 5 c.c. of this substance allowed to volatilise in a closed chamber, such as a rubber bag, into which an adult patient exspires and from which he inspires, produces anæsthesia very rapidly. If administration is then suspended, insensibility lasts from one to two minutes. By administering a further dose before recovery takes place from the first one, anæsthesia can be prolonged; it is preferable, however, to give ether or chloroform or nitrous oxide and oxygen if a longer anæsthesia is required. The after-effects of ethyl chloride are intermediate between those of nitrous oxide and those of ether and chloroform. Ethyl chloride given by an expert is safer than either of the latter, but not so safe as nitrous oxide.

Ether.—About 30 p.c. of air and 70 p.c. of ethereal vapour will produce and maintain general anæsthesia. The vapour is so intensely irritating to the mucous membrane which lines the mouth, nose, and air-passages, that it must first be offered very dilute, and then in a gradually increasing percentage. Limitation of air supply renders it possible to procure anæsthesia with a much smaller quantity of ether than when fresh air is freely admitted, for a slight concurrent asphyxia helps the action of the ether. Such asphyxiation has disadvantages of its own if allowed to exceed a very moderate degree; it is usually present during anæsthesia under ether by the 'closed' methods. There is slightly more difficulty in producing anæsthesia by the 'open' method, in which air enters freely; the preliminary injection of small doses of morphine ($\frac{1}{8}$ to $\frac{1}{4}$ grain) with atropine ($\frac{1}{200}$ to $\frac{1}{100}$ grain) is of advantage. Ether is much less dangerous to life than chloroform in the operating room; but part of this advantage is counterbalanced by the occasional development of bronchitis and broncho-pneumonia afterwards.

Chloroform.—Much research has been carried out to determine the percentage of chloroform necessary to produce anæsthesia by inhalation. Vernon Harcourt introduced early this century a chloroform inhaler capable of regulating this proportion up to 2 p.c. Experience showed that in occasional cases it is very difficult or impossible to induce anæsthesia with this amount, and a modification of the instrument allows air to be inspired containing 3 p.c. In practically every case anæsthesia, when fully established, can be maintained with a 2 p.c. vapour. Alcock, who has investigated the dosage of chloroform very carefully, finds [1] that for an ordinary adult it suffices to offer a percentage rising gradually to $2\frac{1}{2}$ in three minutes; this as a rule produces complete surgical anæsthesia in eight to ten minutes. If a higher proportion is necessary, 3 p.c. may be allowed at the end of five minutes. He finds that within a few minutes after induction is complete 1·5 p.c., and after half an hour 1 p.c., will usually be enough. Several physiologists have estimated the amount of chloroform in the circulating blood during

[1] Laurence Turnbull, Artificial Anæsthesia, 223.
[2] Reicher, Lancet, Jan. 25, 1908, 268.
[3] R. Gill, The $CHCl_3$ Problem, 1906.
[4] Wallace and Gillespie, Lancet, Dec. 5, 1908, 1665

[1] N. H. Alcock, British Medical Journal, Feb. 6, 1909, 325.

anæsthesia : their results vary from 0·035 to 0·07 p.c. Chloroform is the most dangerous of these four anæsthetics, especially in the hands of those whose experience as anæsthetists is small. H. R.

ANALGESINE. Identical with antipyrine (*q.v.*).

ANALYSIS. Chemical analysis is the separation of a complex material into simpler constituents. It is *ultimate* when these component parts are elementary forms of matter, and *proximate* when the subdivision consists only in the separation of the original substance into less complicated compounds. The aim of chemical analysis is twofold : the first object is to ascertain the nature of the components of a mixture or complex substance; the second is to determine the proportions in which these constituents are present. All analytical operations may therefore be classified under the two main categories of *qualitative* and *quantitative* analysis, according as to whether these processes lead to the identification of the proximate or ultimate constituents of a complex substance, or to the determination of the relative proportions in which these constituents are present.

This article is written primarily from the technical point of view, and accordingly the descriptions given in the qualitative section are restricted mainly to those elements which find application in the arts and industries. Similarly, the estimations and separations outlined in the quantitative section are chiefly those required in the analysis of technically important materials.

The systematic investigation of the individual elements and their typical compounds has revealed the existence of many characteristic reactions which are exhibited by certain elements and compounds under widely varying conditions of combination or association. This circumstance leads to a simplification which is utilised extensively in both qualitative and quantitative analysis. In qualitative work, such characteristic reactions as are not generally interfered with by other substances enable the analyst to detect the presence of certain elementary or compound substances without undertaking the more laborious processes involved in isolating these constituents from the other ingredients of a mixture.

In quantitative analysis two essentially different methods of procedure are employed, the more fundamental one being *gravimetric* analysis, in which the elementary or complex constituent of a mixture is isolated and weighed in the form of a definite compound. By utilising quantitatively the above-mentioned distinctive reactions it is frequently possible to adopt the second procedure known as *volumetric* analysis, in which the relative amount of a certain constituent is estimated in the presence of other elements and compounds associated with this constituent in the mixture under examination.

For the purposes of scientific investigation the most accurate methods are essential, and these are, in the main, gravimetric in character ; but for technical requirements extreme accuracy is rarely required, and rapid methods giving approximately correct results are preferred to more exact processes involving

longer time for their execution. It is in this direction that volumetric analysis has been most extensively developed, the general tendency in industrial laboratories being to replace gravimetric methods by quicker volumetric processes with very little loss in accuracy, provided that certain essential conditions be fulfilled.

General Operations.

Sampling.—It is of the highest importance that the sample under examination should be truly representative of the bulk of the substance. Discrepancies between the results of different analysts are usually attributed to faulty methods or inaccurate work, but in many cases they are really due to imperfect sampling. If the substance is a liquid, the contents of the vessel should be thoroughly mixed before the sample is withdrawn. If the substance is contained in several vessels, a proportional quantity should be taken from each, the different portions mixed together, and the final sample taken from the mixture.

In the case of solid products care must be taken to secure a proper proportion of large and small, hard and soft fragments. If a ship's cargo is to be sampled, portions should be taken from different parts of the bulk ; if the substance is contained in railway trucks, portions should be taken from the ends and middle of each truck. When the substance is in bags or barrels, a long hollow auger is thrust to the bottom of each and then withdrawn, bringing with it a long core of the substance. If the material loses or gains moisture, or undergoes any other change on exposure to air, as in the case of soap or caustic soda, a proper proportion of the internal and external portions must be taken. In all cases the first samples are broken into small pieces, thoroughly mixed, and one-fourth taken for further treatment. This is ground to powder, again thoroughly mixed, and one-fourth taken. The subdivision is repeated, if necessary, and the final sample kept in well-closed bottles. This process of 'quartering' may also be effected by spreading out the finely powdered material in the form of a flattened cylinder dividing this radially into four parts, taking out the opposite sectors, mixing these thoroughly, and repeating the subdivision.

If the mixture is soft and friable, pulverisation is readily effected in a porcelain or earthenware mortar, but harder substances should be powdered in a cast-iron or steel mortar. When the substance is hard, and a very fine powder is required, an agate mortar should be used for the final operation, so that the powder may be completely sifted through fine muslin. Very hard substances, such as minerals, are first broken into small pieces by wrapping them in paper and striking with a hammer, and are then further crushed in a steel mortar (Fig. 1) consisting of a strong base with a circular recess into which fits a movable steel ring or guard, and inside this is a solid steel piston which acts as a pestle. A small quantity of the mineral is placed on the base of the mortar inside the guard-ring, the
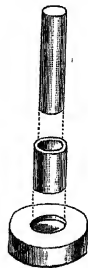
FIG. 1.

latter is held firmly down, and the piston is placed inside and struck smartly with a hammer, which drives it down upon the mineral. The final crushing is done in an agate mortar.

The mechanical ore-grinder described in Hillebrand's Analysis of Silicate and Carbonate Rocks, may likewise be employed in reducing hard minerals to a fine powder.

Drying.—Many substances absorb more or less moisture when exposed to the air, and in order to bring them into a definite condition for analysis, it is desirable that they should be dried, this operation being conducted at the ordinary or at a higher temperature according to circumstances. Substances which contain water in combination are usually dried by exposure to air or by pressure between folds of filter paper. In other cases where a higher temperature would be injurious the substance may be placed under a bell-jar which also incloses a dish containing sulphuric acid. The operation proceeds more quickly if the bell-jar is connected with an air-pump and thus rendered vacuous.

Substances which do not decompose at 100° are best dried in a copper oven provided with a jacket containing water which is heated to boiling, the water-level being kept constant by means of an overflow a and feeding arrangement
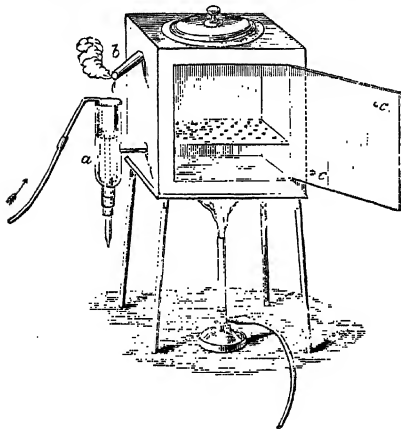
Fig. 2.

at the side. The inside of the oven is fitted with a perforated shelf which supports dishes, funnels, &c. (Fig. 2).

When the substance is sufficiently stable it is advisable to dry at 115°–120°, since an increase of 10° or 20° often greatly reduces the time required. For this purpose we use a copper oven without a jacket, heated by a lamp underneath; or toluene, boiling at 110°, may be used instead of water in the oven with a jacket; crude xylene will give a higher temperature (129°). Inside the oven at a little distance from the bottom is a shelf which supports the vessel containing the substance. At the top of the oven are two apertures, one of which serves to promote a current of air through the oven, whilst the other carries a thermometer the bulb

of which is close beside the vessel which is being heated.

If it is desired to keep the temperature constant for a long time, the oven must be provided with a thermoregulator (*v.* THERMOREGULATORS).

Weighing.—The balance and the precautions to be observed in weighing form the subject of a special article (*v.* BALANCE). As a rule, substances taken for analysis should be weighed from tubes provided with well-fitting stoppers or corks, or from weighing bottles fitted with glass capsule stoppers, the difference between the weight of the tube or bottle before and after the removal of the substance giving the weight taken for analysis. The quantity required for an analysis will depend upon circumstances. When constituents present in minute quantity have to be estimated, a relatively large amount of the substance is required, but for the estimation of one or two constituents from 1 to 2 grams of the substance is usually sufficient. The smaller the quantity of matter operated upon, the shorter the time required for filtration, washing, &c., but also the greater the demands on the skill and accuracy of the operator.

Hygroscopic substances and precipitates must be kept under a *desiccator* (*q.v.*), *i.e.* a glass dish containing sulphuric acid or calcium chloride, fitted with a tray to support a crucible, &c., and provided with an air-tight glass cover, preferably bell-shaped. Crucibles containing non-hygroscopic precipitates may be allowed to cool with exposure to air, provided that the empty crucibles were allowed to cool under the same conditions before weighing.

Solution.—The solution of a substance is most conveniently effected in flasks or in somewhat deep beakers which are inclined at an angle in order to prevent possible loss by spurting. The operation may be accelerated by heat, and the reagent should be used in the most concentrated form possible and in the least possible excess, in order to avoid loss of time in evaporation, &c. Evaporation to expel excess of solvent should, where possible, be conducted in the same vessel.

Evaporation.—The evaporation of a liquid may be effected over an ordinary bunsen flame, or over a rose burner, care being taken that the liquid does not boil. If the operation is conducted in a flask or crucible, the latter should be inclined in order to prevent loss by ebullition, and the operation is accelerated in the first case by drawing a current of air through the flask, in the second by inclining the lid of the crucible (Fig. 3) across the mouth of the vessel and thus producing a circulation. The rate of evaporation, *cæteris paribus*, depends on the area of surface exposed, and hence the operation is effected most quickly in shallow dishes, especially if a current of air removes the vapour as fast as it is given off. During the process the contents of the dish should be protected from dust, &c., and this is really done by supporting at a distance of about six inches above the surface of the dish a triangle of glass rod or tubing on which is stretched a sheet of filter paper freed from soluble compounds by treatment with acid. When evaporation over a direct flame is impracticable, the dishes, &c., should be placed on a *water-bath*, that is, a vessel containing boiling water, in such a way

[2]that they are heated by the steam. The top of the water drying-oven already described (Fig. 2) may be provided with a series of rings of various
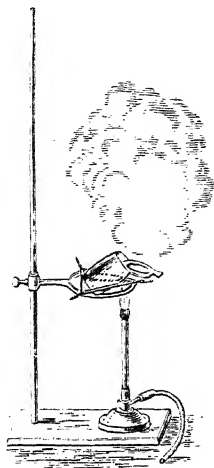
FIG. 3.

sizes and thus serves two purposes. Ordinary tin cans or copper vessels of similar shape will answer, but in all cases it is desirable to have an arrangement for keeping the water at a constant level.

Precipitation is conducted in beakers, dishes, or conical flasks, but not in ordinary round flasks because of the difficulty of removing the precipitate. Glass vessels, especially when new, are appreciably attacked and dissolved by water, and still more strongly by alkaline solutions, the action increasing with the concentration of the solution and the duration of contact. For quantitative work Jena glass vessels should be used, as these are least affected by alkalis. Acid liquids, with the exception of dilute sulphuric acid, have less solvent action. Porcelain vessels, especially after they have been used for a short time, are not appreciably attacked (Fresenius's Quant. Anal.). All precipitations involving long heating with alkaline liquids should be conducted in porcelain vessels or in platinum, silver, or nickel dishes. Silica-ware vessels can be used with all acid liquids excepting those evolving hydrogen fluoride (Zeitsch. anorg. Chem. 1905, 44, 221).

Unless circumstances forbid, the liquid and the reagent should be heated to boiling and mixed gradually with continual agitation, since under these conditions precipitation as a rule is more rapid and complete, and the precipitate is obtained in a dense and granular form and is readily separated and washed. Usually filtration may be commenced as soon as the supernatant liquid is clear, or at any rate after two or three hours. An unnecessary excess of reagent should always be avoided, but in all cases complete precipitation should be proved by adding a small quantity of the reagent to the clear liquid.

Filtration.—The separation of a precipitate from a liquid is usually effected by means of a specially prepared variety of blotting paper, known as filter paper. The Swedish paper made by J. Munktell has the oldest reputation, but that made by Schleicher and Schull, of Düren, is of excellent quality, and for many purposes answers better. The latter firm supply paper which has been treated with hydrochloric and hydrofluoric acids, and thus freed from almost all inorganic matter. Filter papers of similar quality are also supplied by Max Dreverhoff, and by Baker and Adamson. It is desirable that all paper used in quantitative work should be free from soluble compounds, and this end is secured by soaking the ordinary filter paper for three or four hours in pure hydrochloric acid diluted with 15–20 times its volume of water, and then washing thoroughly to remove all traces of acid and soluble salts. The paper is conveniently kept in circular pieces of known radii (2, 4, 5, 6, 8 cm.), and the ash left by each size should be determined once for all by incinerating six filters of one of the medium sizes in the manner described under the treatment of precipitates, and weighing the ash which is left. This quantity divided by six gives the average amount of ash left by one filter of that size, and the amount left by the other sizes is readily calculated. the quantity of ash being proportional to the area of the paper.

Usually the filter paper is supported in a glass funnel which should have smooth even sides and an angle of 60°. The stem should be somewhat long and not too wide, with the lower end cut obliquely. A circular filter is folded in half, then in a quadrant, and when the quadrant is opened at one side it forms a hollow cone which should fit accurately into the funnel. The edge of the filter paper should be about 10 mm. below the edge of the funnel, and the size of the filter should be such that it is not more than three quarters filled by the precipitate. After placing the filter in position it is moistened with water, and fitted accurately to the glass, care being taken to remove all air bubbles from between the glass and the paper. Attention to these points greatly facilitates the subsequent filtration. The edge of the vessel containing the liquid to be filtered is slightly greased outside, and the liquid is directed into the filter by means of a glass rod, care being taken not to disturb the precipitate until most of the clear liquid has passed through. It is advisable to keep the filter well filled with the liquid, but the latter must not rise higher than 10 mm. below the top of the paper.

In order to accelerate filtration a glass tube about 3–4 mm. in diameter and not less than 20 cm. long, bent into a loop near its upper end, may be attached to the stem of the funnel by means of indiarubber tube.

Greater rapidity of filtration is obtained by using one of the numerous water pumps (*v.* FILTER PUMP). In this case the liquid is filtered into a flask with stout walls, preferably of the conical form. The stem of the funnel passes through a cork which fits in the neck of the flask and also carries a tube connected with the pump, or the flask may be provided with a side tube for this latter purpose. When it is required to filter into a dish or beaker, the latter is placed

under a tubulated bell-jar standing on a glass plate, the cork carrying the funnel, &c., being fitted into the tubulus of the bell-jar. If the reduction of pressure is considerable, it becomes necessary to support the apex of the filter. In the case of filters of medium size the necessary toughness is obtained by dropping into the apex of the dry filter, after it has been fitted into the funnel, two or three drops of the strongest nitric acid. After a minute or two the paper is washed and is ready for use. Bunsen's original method is to support the apex of the filter by means of a cone of platinum foil, which is made in the following way. A circular piece of thin platinum foil 3–4 cm. in diameter is cut in the manner shown in the diagram (Fig. 4), softened by heating in a flame, and then placed against a small metal cone of 60°, so that the point a coincides with the apex of the cone. The foil is then folded round the metal so that it also forms a small cone, which is finished by being pressed in a hollow conical mould into which the metal cone fits. It is then dropped into the funnel and the paper fitted in. The metal cones and moulds required can be purchased; Bunsen's method of making a cone and mould of plaster is described in Thorpe's Quantitative Analysis.
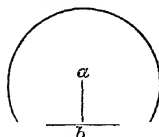
FIG. 4.

Carmichael has described a method of reverse filtration (Zeitsch. anal. Chem. 10, 83).

The Gooch crucible (Chem. News, 37, 181), which has a perforated bottom lined with a thin asbestos mat, has now become a recognised means of collecting precipitates. The asbestos makes an excellent filter, is not affected by ordinary acid and alkaline liquids, is readily dried, and does not alter in weight when ignited. The quality of the asbestos is of prime importance, a non-ferruginous amphibole being preferable to the cheaper hydrated varieties of serpentine which are appreciably soluble in acids. Silky asbestos is scraped into a short fine down, boiled with hydrochloric acid, well washed, and kept in water. A platinum or silica crucible, preferably of the low wide form, with the bottom perforated with a large number of minute holes, is fitted air-tight into an ordinary funnel by means of an indiarubber ring placed between the crucible and the wall of the funnel, which is fitted into a filtering flask. The pump is set in action and water containing the asbestos in suspension is poured into the crucible. A layer of asbestos felt is quickly formed, and when this is of sufficient thickness it is drained, dried, and ignited over a lamp, and the crucible is then weighed. It is desirable to have a non-perforated bottom to fit on the crucible during ignition, in order to protect the contents of the crucible from the flame gases. A Soxhlet tube, having a perforated porcelain or platinum disc covered with an asbestos layer and supported at the constricted part of the tube, is frequently used to collect precipitates. Neubauer recommends a perforated platinum crucible with a felted platinum mat (Zeitsch. anorg. Chem. 1901, 922; cf. Amer. Chem. J. 1909, 31, 456). The weighed crucible is replaced in the funnel, and filtration is conducted in the ordinary way,

care being taken that the pump is set in action before any liquid is poured into the crucible. Drying and igniting the precipitate occupies but little time. For gelatinous precipitates the crucible may be replaced by a cone, the lower part of which is made of platinum gauze and the upper part of platinum foil.

Gooch has proposed (P. Am. A. 1885, 390 ; Zeitsch. anal. Chem. 24, 583) in special cases to replace the asbestos by anthracene, which after filtration can be dissolved in benzene or other suitable solvent, leaving the precipitate undissolved.

Not unfrequently it is necessary to keep the contents of a funnel hot during filtration. This is effected by placing the funnel inside a copper jacket filled with water which is heated to boiling by means of a side tube. A simpler plan is to coil lead pipe round the funnel and blow steam through the pipe (Richter, J. pr. Chem. (ii.) 28, 309).

Sometimes it is desirable to avoid contact with air during filtration. A convenient apparatus for this purpose has been described by Klobukow (Zeitsch. anal. Chem. 24, 395 ; J. Soc. Chem. Ind. 4, 756).

All precipitates require to be washed in order to remove soluble impurities, the liquid employed being water, dilute acid, dilute ammonia, alcohol, &c., as the case may require. The object in all cases is to reduce the impurity to the desired minimum in the shortest possible time with the least expenditure of liquid, and it can readily be shown that successive treatments with small quantities of the liquid are far more effectual than the same volume of liquid applied all at once (Bunsen, Annalen, 148, 269). Whenever possible hot liquids should be used, and the precipitate should be washed so far as possible by decantation, only the washing liquid being poured on the filter. The soluble impurity collects round the top edge of the filter paper by reason of capillary action and evaporation, and hence, when washing is effected with the aid of an ordinary wash-bottle with a movable jet, it is important that the liquid should be directed on to the top edge of the filter. It is also important that each quantity of wash-water should be drained away as completely as possible before adding a fresh quantity, and it is obvious that this takes place most readily when a pump is used. In this case the liquid is poured into the funnel from an open vessel to a height of about 10 mm. above the edges of the paper. Care must be taken that the precipitate is not drained so far that channels are formed. It is always advisable to ascertain whether the washing is complete by testing a few drops of the last wash-water.

Drying and weighing precipitates.—Occasionally a precipitate must be dried without the application of heat, and this is accomplished in a desiccator over sulphuric acid, preferably in a vacuum. In other instances the substance is not injured by a temperature of say 120°, but cannot be ignited. In these cases the filter is carefully dried at the particular temperature, enclosed between a pair of watch-glasses, and weighed. It is then placed in the funnel and the operation proceeded with. After filtration the filter and the precipitate are thoroughly dried at the same temperature as before and

again weighed, the increase being the weight of the precipitate. Tared filters can, however, be generally replaced by Gooch crucibles, Soxhlet tubes, &c. The majority of the precipitates usually met with can, moreover, be dried by heating them in a crucible over a lamp. In most cases it is not necessary that the precipitates should previously be dried. The greater part of the water is removed by draining in the funnel by means of the pump or by placing the filter and its contents on a porous tile or on a pad of filter paper. The filter is then introduced into a crucible, heated cautiously until quite dry and then heated more strongly until the weight is constant.

When the precipitate is not easily reducible it is not necessary to remove the paper before ignition. The wet paper enclosing the precipitate is placed in a platinum crucible, the latter heated with a full flame; the water present assumes the spheroidal state and the paper smoulders away without spurting. If any slight reduction takes place, for example, with barium sulphate, it is easily remedied by adding a few drops of dilute sulphuric acid and again heating. In the case of magnesium pyrophosphate strong nitric acid serves a similar purpose. If, however, the precipitate is readily reduced in contact with organic matter, it must be removed from the paper as completely as possible by gentle friction, and transferred to the crucible, which should stand on a sheet of glazed paper. A carefully trimmed feather or a camel's-hair brush is useful to transfer scattered particles from the paper to the crucible. The filter paper is then folded with the portion to which the precipitate had adhered inside, wrapped in platinum wire which forms a sort of cage, and set on fire. Whilst burning it is held over the crucible, and *when completely burnt out*, the ash is heated with the tip of a Bunsen flame for a few minutes and then shaken into the crucible.

Precipitates which contain compounds of silver, lead, zinc, tin, and other easily reducible metals, should be heated in porcelain crucibles, since platinum vessels are liable to be attacked. Care should also be taken that platinum vessels are not heated with smoky or 'roaring' flames, and do not come in contact with brass crucible tongs or easily fusible metals whilst hot. After some time the surface of the metal may become dull, owing to the partial disaggregation of the platinum, but this defect can be remedied by polishing the metal with sea-sand or a burnisher.

Heating appliances.—The ordinary bunsen burner serves for most operations, but the argand bunsens introduced by Fletcher are more efficient, and the radial slit burner of the same inventor is perhaps the most efficient gas-burner for heating purposes that has yet been made. Glass vessels are more safely heated on a sheet of wire gauze or on a layer of sand in a metal tray. A most useful piece of apparatus in a technical laboratory is a large iron plate supported on iron legs, and heated by a burner underneath the middle. Vessels placed on the plate near its edges are subjected to a very gentle heat, but may be raised to a much higher temperature by being moved nearer to the middle.

A water-bath provided with a constant feeding arrangement is the most useful way of heat-ing vessels at 100°. If higher temperatures are needed, a saturated solution of calcium chloride, melted paraffin, or oil may be used. Maumené (Compt. rend. 1883, 97, 45, and 215) has proposed to use fused mixtures of alkaline nitrates for temperatures between 140° and 250°. Brauner (Chem. Soc. Trans. 1885, 47, 887) has described a simple arrangement for heating substances in sulphur vapour.

Reagents.—The ordinary acids and ammonia are required in a dilute as well as in a concentrated form. Whenever possible the reagents should be made in solutions the strengths of which are multiples or submultiples of normal solutions. A convenient strength for the dilute mineral acids is twice normal, and the alkaline solutions should be of equivalent strength.

QUALITATIVE ANALYSIS.

The detection of the constituents of a mixture or chemical substance is based on the fact that almost every metallic or acidic radicle will under suitable conditions give rise to a reaction which, under these conditions, is characteristic and thus enables one to distinguish this radicle from all others. These tests may be applied directly to the solid substance, usually at high temperatures, when they are known as *dry reactions ;* or they may be employed in solution, in which case they are described as *wet reactions.* The wet and dry reactions of metallic and acidic radicles are generally, but by no means invariably, independent of the acidic and metallic radicles with which they are respectively combined.

Examination in the Dry Way.

The indications obtained from the dry reactions of a substance frequently afford very suggestive clues to its composition, but as these tests rarely, if ever, indicate the relative proportions in which the constituents exist in the mixture under examination, they must be regarded as being preliminary to the more systematic examination of the substance in solution. Moreover, negative results obtained from dry tests must not be accepted as final evidence.

In all cases, however, a preliminary examination of the substance should be made in the dry way, and if the substance is in solution a portion should be evaporated to dryness. The reactions of several substances in the dry way are interfered with and rendered inconclusive by the presence of certain other substances ; but nevertheless an examination of this kind often gives much information in a short time.

The most convenient source of heat for this purpose is the ordinary bunsen burner. This consists of a metal tube at the base of which coal gas enters by means of a jet, the lower part of the tube being pierced with holes through which air is drawn and mixed with the coal gas. The mixture of 1 volume of coal gas with about 2½ volumes of air, which is thus produced, burns at the top of the tube with a non-luminous flame. When the supply of gas is turned low, it is necessary also to reduce the air supply by partially closing the inlet holes by means of a regulator. The upper part of the burner is generally fitted with a support carrying a cone to protect the flame from draughts.

The flame consists essentially of an inner

dark zone containing unburnt gas mixed with air, and an outer zone or flame mantle in which combustion becomes complete. If the air holes are partially closed, a luminous cone appears at the top of the inner zone. Bunsen has shown, however, that several distinct zones exist, each of which can be utilised for producing particular reactions. The most useful of these are α, a comparatively cold zone at the base of the flame, which serves for the volatilisation of salts in order to obtain flame colourations; the *lower reducing flame* δ about one quarter of the way up and close to the edge of the dark zone; η, the *upper* and more powerful *reducing flame* at the top of the dark zone, obtained by closing the air holes until the tip of the inner zone just becomes luminous; β, the *zone of fusion* or highest temperature, at about one-third the height of the flame and half-way between the inner zone and the flame mantle; γ, the *lower* and hotter *oxidising flame* at the edge just below the zone of fusion; and ε, the *upper oxidising flame* at the extreme tip of the flame.

Fig. 5.

Instead of the bunsen burner, the flame obtained by means of a blowpipe may be used; a mouth blowpipe consists of a metal tube provided at one end with a mouthpiece, the other end fitting into a small metal box which serves to condense and retain the moisture of the breath. From the side of this box a second shorter and narrower tube projects at right angles to the first, and is provided with a nozzle or jet of brass or, better, of platinum. For general work the diameter of the bore of the jet should be

Fig. 6.

0·4 mm. In Black's blowpipe the larger tube is conical, the lower and wider end serving the same purpose as the box in the form just described. The art of keeping up a continuous blast of air through the blowpipe can only be acquired by practice. The necessary pressure is produced by distending the cheeks, breathing being carried on through the nostrils, whilst communication between the nostrils and the mouth is cut off by the pressure of the tongue against the palate. A convenient form of hand-blower for blowpipe work has been devised by Fletcher.

A good flame for blowpipe work is obtained by dropping into the tube of an ordinary bunsen burner a brass tube, the lower end of which descends to the bottom of the burner and cuts off the supply of air, whilst the upper end is flattened and cut off obliquely. The flame should be much smaller than when the burner is used in the ordinary way. Coal gas usually contains more or less sulphur, and consequently cannot be used when testing for this element.

A thick stearin candle answers well; but nothing is better than a lamp consisting of a low and rather wide cylindrical metal vessel, open at the top, with a somewhat broad and flat wick-holder attached to the side. The fuel used is solid paraffin, which is kept in a melted condition by the heat of the blowpipe flame, the wick being so arranged that the flame passes over the top of the paraffin. A metal cover protects the lamp from dust when not in use.

The nozzle of the blowpipe is introduced a short distance into the lamp flame at a short distance above the wick, and when the blast is produced the flame is deflected horizontally, becomes long and narrow, and is seen to consist of two parts, viz. an *outer* or *oxidising* flame, at the tip of which there is an excess of oxygen

Fig. 7.

heated to a high temperature, and an *inner* or *reducing* flame, which contains carbonic oxide and hydrocarbons heated to a high temperature. If the blowpipe is held just at the edge of the flame and a moderate blast is used, a broader reducing flame can be obtained, which has a luminous tip containing solid particles of carbon.

The following appliances are required: a small pair of forceps with platinum points; short pieces of thin platinum wire; charcoal from some fine-grained compact wood; glass tubes about 3 mm. internal diameter, and 60–80 mm. long, closed at one end; and glass tubes of similar diameter 100–120 mm. long, open at both ends and bent slightly in the middle. The reagents used are borax, microcosmic salt (NH_4NaHPO_4, $4H_2O$), potassium cyanide, sodium carbonate, potassium nitrate, cobalt nitrate solution, and potassium hydrogen sulphate.

The dry tests are conveniently performed in the following order:—

(1) *Heating in a dry closed tube.*—To avoid soiling the sides of the tube, the substance should be introduced by means of a roll of stiff paper. The following changes may be observed:

(a) Carbonisation with or without evolution of empyreumatic vapours = *organic compounds*.

(b) Condensation of moisture on cold part of tube; neutral reaction = *hydrated salts and hydroxides*; acid reaction = *acids and acid salts*; alkaline reaction = *ammonium salts*.

(c) Fusion without change of colour = *alkaline salts, hydrated salts*.

(d) Fusion with change of colour = yellow hot, dark yellow cold = *bismuth oxide*; yellow hot, red cold = *lead oxide*. The chromates of lead and the alkali metals fuse and darken on heating.

(e) No fusion, but change of colour: dark yellow hot, pale yellow cold = *stannic oxide*; yellow hot, white cold = *zinc oxide*; black hot, reddish-brown cold = *ferric oxide*; black hot, bright red cold = *mercuric oxide*; brown darkening on heating = *cadmium oxide*.

M 2

(f) Gas evolved: oxygen=*oxides, peroxides, chlorates, bromates, perchlorates, iodates, periodates, persulphates,* and *nitrates*; carbon dioxide = *carbonates, bicarbonates, oxalates*; carbon monoxide (blue flame) = *formates, oxalates*; sulphur dioxide ... *acid sulphites, sulphates of heavy metals, together with sulphur trioxide,*: cyanogen = *cyanides of heavy metals*; ammonia = *ammonium salts*; phosphine = *phosphites, hypophosphites*; orange-brown vapours = *nitrates, nitrites, bromides*; violet vapours = *iodides*; colourless fuming gas = *hydrated chlorides.*

(g) Sublimate: white infusible = *arsenious oxide* (octahedra), *antimonious oxide* (needles), *selenium dioxide, ammonium chloride, ammonium sulphite* (from ammonium sulphate); white fusible = *mercuric chloride, tellurium dioxide, organic acids, molybdenum trioxide* (at very high temperatures); coloured, black, or reddish black = *selenium, mercuric sulphide*; yellow hot, red cold = *mercuric iodide*; reddish yellow = *arsenious sulphide*; yellow = *sulphur and sulphides*; black metallic mirror = *arsenic*; grey metallic globules = *mercury.* These metallic sublimates are often obtained nore readily by heating the material with potassium cyanide.

Phosphorus compounds are detected by heating in a closed tube with magnesium ribbon and dropping the hot tube into water, when inflammable phosphine is evolved.

(2) *Heating in open tube.*—The tube being inclined, to promote a current of air through it, the changes observed are similar to the reactions in the closed tube, but sulphides burn evolving sulphur dioxide; arsenic is oxidised to arsenious oxide, and selenium and its compounds evolve a pungent odour of horse-radish (dioxide), and give a grey or reddish sublimate.

(3) *Heating on platinum wire.—Flame colourations.*—The wire being cleaned by repeated dipping in hydrochloric acid and heating till it imparts no colour to the flame, a small quantity of the substance supported on the end of the wire is introduced into zone *a* of the bunsen flame. As a colouration is produced only if volatile compounds of the metals are present, the substance should be moistened with hydrochloric acid to produce the volatile chlorides. This result may also be attained by mixing the substance on an asbestos thread with moist silver chloride, a compound which, while imparting no colour to the flame, slowly yields chlorine, converting other metals into chlorides. The wire should be slowly moved into the hottest part of the blowpipe or bunsen flame, so that the colourations due to less volatile constituents may be successively developed.

Colourations: yellow = *sodium*; orange red = *calcium*; crimson = *strontium, lithium*; lavender = *potassium, rubidium, cæsium*; apple green = *barium*; bright green = *thallium, copper, boric acid*; pale blue = *lead, antimony*; deep blue becoming green = *copper halides*; deep blue = *selenium.*

The pocket spectroscope (direct vision) is a useful aid in examining flame colourations, particularly in the case of strontium and calcium, which exhibit respectively a characteristic blue and a yellowish-green line.

(4) *Heating on charcoal.*—The substance mixed with three times its weight of dry sodium carbonate or of a mixture of 2 parts sodium carbonate and 1 part potassium cyanide, is placed in a small shallow hole scooped out in charcoal, and heated in a reducing flame. The metallic bead obtained is examined as to colour, malleability, solubility, &c. Many metals yield films of oxide, which coat the charcoal at a greater or less distance from the flame, and the colour and appearance of which are more or less characteristic. These and similar films are best seen when the charcoal is supported on an aluminium plate (Ross). A piece of sheet aluminium 12 cm. by 5 cm. is bent in right angles at a distance of 2 cm. from one end, thus forming a ledge on which a small flat piece of charcoal is placed, the plate being held so that the surface rises vertically behind the ledge. Volatile oxides, &c., condense on the metallic surface (*v.* Hutchings, Chem. News, 1877, 36, 208, 217).

The reduction may also be effected by adding a fragment of sodium to the substance supported on charcoal (Parsons, J. Amer. Chem. Soc. 1901, 23, 159).

In order to obtain reduced metals with the bunsen flame, a match-stick is smeared with ordinary sodium carbonate (washing soda) which has been melted by holding it in the flame, and the wood thus prepared is carbonised by heating it in the flame. A small quantity of the substance is mixed in the palm of the hand with a small quantity of the fused washing soda, and the mixture is carefully placed on the charcoal splint, which is then heated in the lower or upper reducing flame. When reduction is complete, the match is allowed to cool inside the dark zone, and is then withdrawn, crushed in a mortar, and the lighter particles of charcoal removed by levigation with water, the heavy metallic particles being left.

By means of the bunsen flame reduced metals and their oxides can be obtained in the form of films on a porcelain surface. The substance is supported on a long slender piece of asbestos, and heated in the tip of a small oxidising or reducing flame, a small evaporating dish containing cold water being held momentarily just above the asbestos (*v.* Bunsen's Flammen-reactionen, Heidelberg, 1880).

Incrustations on charcoal: white, very volatile = *arsenic*; white, less volatile = *antimony*; orange-yellow hot, pale yellow cold = *bismuth*; pale yellow hot, deep yellow cold, white edge = *lead*; yellow hot, white cold = *zinc, molybdenum*; reddish-brown or orange-yellow cold = *cadmium.*

Metallic beads or residues on charcoal: white malleable = *silver, tin, lead*; red malleable = *copper*; grey brittle = *antimony, bismuth*; grey powder, magnetic = *iron, cobalt, nickel*; non-magnetic = *molybdenum.*

(5) *Cobalt nitrate reactions.*—Certain infusible substances, when moistened with cobalt nitrate solution and strongly heated, acquire characteristic colours. These reactions are frequently, but not necessarily, carried out on a charcoal support:—blue infusible mass = *aluminium*; blue fusible = *certain phosphates, silicates, borates*; green = *zinc, titanium, tin*; pink = *magnesium.*

(6) *Heating with borax or microcosmic salt.*— A small loop is made at the end of a platinum wire, to which some borax or microcosmic salt is

made to adhere, and heated in the flame until fused. The bead when cold must be quite transparent and colourless, otherwise it must be remelted, shaken off, and a fresh bead made. A *small* quantity of the substance is taken on the bead and heated first in the oxidising flame (O.F.) and then, after it has been examined, in the inner or reducing flame (I.F.). The colour of the bead should be observed both hot and cold. If too much substance is taken, the bead becomes opaque, and the colour cannot be distinguished.

These so-called borax and microcosmic beads owe their colour respectively to the formation of certain borates and phosphates of the heavy metals. Borax glass consists of anhydrous $Na_2B_4O_7$, and when heated with a metallic oxide or salt the excess of boric oxide present unites with the metallic oxide, forming the corresponding borate :

$$Na_2B_4O_7 + CoO = Na_2B_2O_4 + CoB_2O_4 \text{ (blue)}.$$
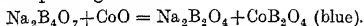
Microcosmic salt on ignition yields the readily fusible sodium metaphosphate, and this salt combines with metallic oxides to form double orthophosphates :

$$NaPO_3 + CuO = CuNaPO_4 \text{ (green)}.$$
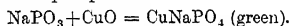
When a silicate is introduced into the molten metaphosphate, the latter withdraws the basic oxide from the former, setting free silica, which remains undissolved ('silica skeleton') :

$$CaSiO_3 + NaPO_3 = CaNaPO_4 + SiO_2.$$
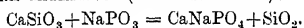
Borax beads.—

	Inner flame		Outer flame		Metal
Hot	Cold	Hot		Cold	
Green	Bottle-green	Yellow	Paler		*Iron*
Green	Green	Yellow	Green		*Chromium*
Green	Bottle-green	Yellow	Pale yellow		*Uranium*
Colourless	Colourless		Amethyst	Amethyst	*Manganese*
Blue	Blue	Blue	Blue		*Cobalt*
Grey	Grey	Violet	Reddish-brown		*Nickel*
Brownish	Emerald-green	Yellow	Greenish-yellow		*Vanadium*
Colourless	Brown	Green	Bluish-green		*Copper*
Colourless	Colourless	Orange-red	Colourless		*Cerium*
Brown	Brown	Yellow	Colourless		*Molybdenum*
Brownish-violet		Yellow	Colourless		*Titanium*
Yellow to brown		Yellow	Colourless		*Tungsten*

*Microcosmic beads.—*The colours produced are similar to those in the borax bead, but the reducing-effects are less pronounced. In the I.F. molybdenum compounds give a green colour, and those of tungsten a greenish-blue tint. Chlorides and bromides evolve a blue and green flame when heated with a microcosmic bead saturated with copper oxide, and iodides give a green flame.

(7) *Other special dry tests.—*(*a*) Heating on charcoal with potassium (or cuprous) iodide and sulphur : crimson incrustation = *bismuth* ; lemon yellow incrustation = *lead* ; greenish-blue fumes = *mercury*.

(*b*) Heating on charcoal with (i.) fusion mixture (Na_2CO_3, K_2CO_3) alone and moistening with dilute acid, hydrogen sulphide evolved = *sulphur compounds* ; (ii.) fusion mixture and sulphur, soluble mass giving coloured precipitate with dilute acid, yellow = *tin* ; orange = *antimony*. The fused insoluble oxides SnO_2 and Sb_2O_4 can be thus characterised.

(*c*) Heating with fusion mixture and potas-sium nitrate : soluble green mass = *manganese* ; yellow mass = *chromium*.

(*d*) Heating in closed tube with potassium hydrogen sulphate. Gas evolved : carbon dioxide = *carbonates, oxalates* ; accompanied by charring of the residue = *tartrates, citrates,* &c. ; carbon monoxide (blue flame) = *formates, oxalates* ; sulphur dioxide = *sulphites, thiosulphates* ; hydrogen sulphide = *sulphides* (not all) ; hydrogen chloride (fuming in air) = *chlorides* (not all) ; hydrogen fluoride (etching glass) = *fluorides* ; bromine and hydrogen bromide = *bromides* ; iodine = *iodides* ; nitrous fumes = *nitrites, nitrates.*

Examination in the Wet Way.

The preparation of the solution requires some attention. A metallic substance is treated at once with moderately strong nitric acid. Tin and antimony form oxides which to a great extent remain undissolved ; arsenic is oxidised to soluble arsenic acid ; other metals (with the exception of gold and the platinum metals, which are not attacked) are converted into nitrates, which dissolve at once or on diluting.

If the substance is not a metal, it is first treated with hot water, and if anything is dissolved (which is ascertained by evaporating a few drops on platinum foil), the substance is boiled two or three times with fresh quantities of water. Any residue which may be left is treated with dilute hydrochloric acid, and afterwards, if necessary, with the concentrated acid. Care must be taken to observe if any gas is given off— *e.g.* carbon dioxide (effervescence), from *carbonates* ; sulphur dioxide, from *sulphites* or *thiosulphates* ; chlorine, from *peroxides* or *hypochlorites* ; hydrocyanic acid, from *cyanides* ; hydrogen sulphide, from *sulphides.* Many chlorides are insoluble in the strong acid, and hence the solution must be diluted before filtering. Silver, lead, and univalent mercury will be converted into insoluble chlorides.

Solvent action of the mineral acids (v. A. A. Noyes and W. C. Bray, J. Amer. Chem. Soc. 1907, 29, 137, 481).—In dealing with substances insoluble in water the following acidic solvents may be used : hydrochloric, nitric, sulphuric, and hydrofluoric acids. Although it is impossible to give a hard-and-fast rule as to the way in which these agents should be applied, the following considerations will indicate the relative advantages of one or other of these solvents :—

Hydrochloric acid.—(1) Advantages : (i.) Solutions on this acid do not yield a precipitate of sulphur on treatment with hydrogen sulphide ; (ii.) the solvent action of this acid on the following oxides : lead peroxide, manganese dioxide, and the hydrated oxides of tin and antimony, is superior to that of nitric acid ; (iii.) hydrated silica is readily precipitated on evaporating the hydrochloric acid solution.

(2) Disadvantages : (i.) This acid is comparatively useless for alloys ; (ii.) evaporation of the hydrochloric acid solution leads to the volatilisation of arsenic, mercury, tin and selenium as chlorides.

Nitric acid.—(1) Advantages : (i.) The best general solvent for the metals and their alloys ; (ii.) oxidises and dissolves insoluble compounds of arsenic, mercury, and selenium without the formation of volatile compounds of these

elements; (iii.) does not cause the precipitation of silver or lead: (iv.) oxidises sulphides not attacked by hydrochloric and sulphuric acids.

(2) Disadvantages: (i.) This acid alters the state of combination of many elements, *e.g.* it oxidises mercurous, arsenious, antimonious, stannous, and ferrous salts; (ii.) its solution deposits much sulphur on treatment with hydrogen sulphide: (iii.) the oxidation of sulphides by nitric acid in the presence of barium, strontium, and lead leads to the precipitation of these metals as sulphates; (iv.) nitric acid is less efficacious than hydrochloric acid in rendering hydrated silica insoluble.

The nitric acid solution of an alloy when evaporated to dryness and heated at 120°–130° may yield the partially dehydrated hydroxides of silica, tin, antimony, titanium, and tungsten in an insoluble condition. When phosphorus or arsenic is present together with tin the so-called stannic phosphate or arsenate (phospho-stannic or arsenostannic acid) may also be found in the insoluble residue.

Sulphuric acid.—The dilute acid is of little value as a solvent, but the hot concentrated acid has been found useful in certain cases. (i.) In bringing certain alloys into solution, *e.g.* white metals (*v.* Low, J. Amer. Chem. Soc. 1907, 29, 66); (ii.) destruction of organic matter; evaporation of a concentrated sulphuric acid solution of the substance is preferable to ignition, because the latter process renders certain compounds insoluble and leads to the loss by volatilisation of such elements as mercury, arsenic, selenium, &c. Very stable organic substances (*e.g.* paraffin and cellulose) can be destroyed completely by adding a little strong nitric acid and heating till the solution acquires a light yellow colour. When diluted considerably with water (20–30 vols.) this solution may yield a deposit containing silica and certain refractory silicates and fluosilicates, together with the sulphates of barium, strontium, lead, calcium, and chromium (an insoluble sulphate formed during the heating), basic sulphates of bismuth, antimony, and tin and the ignited oxides of the last two metals with those of aluminium and titanium. (iii.) Insoluble compound cyanides are decomposed by hot concentrated sulphuric acid, but may also be attacked by aqueous alkali hydroxides yielding soluble alkali cyanides and insoluble metallic hydroxides.

Hydrofluoric acid.—The insoluble residues from the preceding acids may be treated with a 40 p.c. solution of hydrogen fluoride, which is now obtainable in glass bottles lined with paraffin wax. (1) Advantages: (i.) Many insoluble silicates are readily decomposed, the silicon being eliminated completely as gaseous silicon fluoride; (ii.) the reducible metals and their compounds may be treated in platinum basins or crucibles providing that the solution is never evaporated to dryness.

(2) Disadvantages: (i.) Glass or silica-ware vessels cannot be used with hydrofluoric acid; (ii.) owing to the destructive action of hydrogen fluoride on animal tissues, all operations with solutions of this gas must be conducted in an efficient draught cupboard.

Aqua regia (concentrated hydrochloric acid 3 parts and nitric acid 1 part) may be employed in attacking substances not dissolved by hydrochloric or nitric acid, although it is of little use for colourless insolubles. It readily dissolves gold and platinum, but is less efficacious in rendering soluble the rarer noble metals (*e.g.* osmium and iridium).

Treatment of Insolubles.

The substances not dissolved by the foregoing acidic reagents are generally regarded as insolubles, although they are divisible into two classes: (i.) *pseudo-insolubles*, which are dissolved by certain specific solvents; (ii.) *true insolubles*, which are only broken up into soluble compounds by the agency of fused alkali carbonates.

Pseudo-insolubles.—Silver chloride and *bromide*, soluble in aqueous ammonia. (The three silver halides may be completely decomposed by treatment with zinc and dilute sulphuric acid, metallic silver and soluble zinc halide being produced.) *Insoluble fluorides* (those of the common and rare earth metals) are decomposed by heating with concentrated sulphuric acid. *Lead sulphate*, soluble in ammonium acetate solution; *oxides of antimony*, dissolved in hydrochloric and tartaric acids. *Anhydrous chromic sulphate* and *basic bismuth sulphate*, converted respectively into hydroxide and basic carbonate by boiling with aqueous sodium carbonate; these products are then dissolved in dilute mineral acids.

True insolubles.—These substances are fused with a mixture of sodium and potassium carbonates in equimolecular proportions (so-called fusion mixture). In the absence of reducible metals (*e.g.* silver or lead), insoluble sulphates (barium and strontium sulphates) and silicates may be heated with the fusion mixture in a platinum crucible. If any insoluble molybdenum sulphide is present (indicated by dry tests), a little nitre must be added to oxidise this sulphide, and thus prevent its corrosive action on the platinum. In the case of an insoluble silicate the fused mass is treated directly with hydrochloric acid, when the metals present pass into solution as chlorides, and the silica is rendered insoluble by evaporating down the acid solution. In the case of insoluble sulphates the fused mass is extracted with water to remove the soluble alkali sulphate, and the residue $(BaCO_3, SrCO_3)$ is subsequently dissolved in dilute acid.

Silver iodide, bromide, and chloride are decomposed by 'fusion mixture,' yielding the soluble alkali halide; insoluble lead compounds are similarly decomposed. The strongly heated oxides of aluminium, chromium, titanium, tin, and antimony rank as insolubles; they are not readily attacked by 'fusion mixture,' but are rendered soluble by fusion with potassium hydroxide. The oxides of titanium and aluminium may be rendered soluble by fusion with potassium hydrogen sulphate; special methods for treating the insoluble oxides of chromium, tin, and antimony are indicated among the dry tests (7, *b* and *c*). The insoluble compounds of the easily reducible metals (*e.g.* Ag, Pb, Sn, Sb, &c.) can all be decomposed and reduced by fusion with sodium or potassium cyanide.

When both aqueous and acid solutions have been obtained from the same substance, the analyst must use his judgment as to whether

they may be mixed or should be analysed separately. The latter course sometimes gives information as to the distribution of the acids and bases in the original substance. If the first course is adopted, it must be borne in mind that the hydrochloric acid solution may precipitate lead and silver, and possibly mercury, from an aqueous or nitric acid solution.

Systematic Method of Examination in the Wet Way.

The formation of a precipitate at the proper stage in the systematic separation is not sufficient proof of the presence of a particular substance; some characteristic confirmatory test should always be applied. The colour of the solutions at different stages in the operation is a valuable indication. Unnecessary excess of reagents should be avoided, but filtrates should always be tested to make sure that precipitation is complete. Many tests succeed only when the proper proportion of the reagent is added, and it should be a rule always to add the reagents very gradually. All precipitates which have to be subjected to the action of reagents should be carefully washed, but in qualitative analysis it is not as a rule desirable that all the washings should mix with the filtrate.

The reaction of the original solution towards litmus paper should be noted and a portion tested for ammonium compounds by heating with sodium hydroxide or by triturating in a mortar with soda-lime (dry sodium and calcium hydroxides).

In systematic qualitative analysis advantage is taken of certain *similarities* existing between the metallic radicles which enable these radicles to be divided into a limited number of groups, the members of which are subsequently either separated or identified by means of the *differences* between the properties of their respective compounds.

The metallic radicles are divided into six groups, according to their behaviour with the following reagents, which must be applied in the order given. It may be mentioned that some chemists prefer a division into five groups, and add the reagents of Groups III. and IV. successively *without* an intervening filtration. This process is conveniently adopted in the presence of the less commonly occurring metals (J. Amer. Chem. Soc. 1908, 30, 481).

GROUP I.—Reagent: hydrochloric acid in moderate excess. Precipitate: *silver, lead, thallium* (*thallous*), and *mercurous chlorides*; *tungstic acid.*

If the original solution is alkaline, the group precipitate may contain sulphides (*e.g.* As₂S₃, Sb₂S₃, SnS₂) which had been dissolved in aqueous alkali sulphide or hydroxide. This yellow or orange precipitate is examined under Group II. The group precipitate may also contain insoluble silver salts (*e.g.* AgBr, AgI) precipitated from solution in alkaline cyanides or thiosulphates; these are dealt with as insolubles. The filtrate from the Group I. precipitate or the solution itself in the absence of a precipitate, must be evaporated nearly to dryness if nitric acid or nitrates are present, since these compounds lead to the precipitation of sulphur in Group II.

GROUP II.—Reagent: hydrogen sulphide in acid solution. Thioacetic acid has been recommended as a substitute for hydrogen sulphide in qualitative analysis (Schiff and Tarugi, Ber. 1894, 27, 2437). Precipitate: the *sulphides* of *arsenic, antimony, tin, molybdenum, gold, platinum* (*the other platinum metals*), *bismuth, lead, mercury, copper,* and *cadmium,* together with *selenium* and *tellurium,* partly free and partly as *sulphides.* The solution should be dilute and not too acid, and it should be treated and saturated repeatedly with the group reagent, since prolonged treatment is required to precipitate molybdenum and the platinum metals.

The filtrate from the foregoing sulphides is boiled to expel hydrogen sulphide, and any iron present peroxidised by warming with nitric acid or bromine water. If organic matter is present, it is destroyed either by evaporation to dryness or treatment with hot concentrated sulphuric acid (*v. supra*). Silica or barium sulphate may be precipitated at this stage. A portion of the oxidised solution should now be tested for phosphate with nitric acid and ammonium molybdate.

GROUP III.—Reagents: ammonium chloride and ammonium hydroxide. Precipitate: (*a*) In absence of phosphates: *hydroxides* of *aluminium, iron, chromium, glucinum, titanium, zirconium, tantalum, columbium, thorium, cerium* (*and other rare earth metals*), and *uranium* as *ammonium diuranate.* Some manganese, zinc, and alkaline earth metals may be coprecipitated. (*b*) In presence of phosphates: *the phosphates of the preceding metals, together with those of Groups IV., V., and magnesium.*

GROUP IV.—Reagents: ammonium sulphide or hydrogen sulphide and ammonium hydroxide. Precipitate: *sulphides* of *zinc, manganese, cobalt, and nickel.* The precipitation is carried out in the boiling solution, and the filtrate, if brown, is slightly acidified with hydrochloric acid, when *vanadium* and a small portion of the nickel are precipitated as sulphides.

GROUP V.—Reagents: ammonium carbonate and ammonia. Precipitate: *barium, strontium,* and *calcium* as *carbonates.*

GROUP VI.—The filtrate from Group V. contains *magnesium, sodium, lithium, potassium, rubidium,* and *cæsium,* which are identified by special tests.

In the absence of the rarer metallic radicles, the group precipitates are examined in the following manner. Confirmatory tests are given under special reactions.

GROUP I.—The precipitate is boiled with water; the aqueous extract mixed with dilute sulphuric acid gives a white precipitate (PbSO₄), indicating *lead.* The insoluble portion is treated with aqueous ammonia; a black residue (NH₄Hg₂Cl or NH₂HgCl and Hg) indicates *mercury*; the ammoniacal filtrate acidified with nitric acid gives white silver chloride, indicating *silver.*

GROUP II.—The precipitate is washed with aqueous hydrogen sulphide and warmed with yellow ammonium sulphide [(NH₄)₂Sₓ], this extraction being repeated.

(A) The filtrate is acidified with dilute hydrochloric acid, the precipitate boiled with strong aqueous ammonium carbonate, and the solution filtered; the filtrate acidified yields a yellow

precipitate (As_2S_3), denoting *arsenic*. The residue is dissolved in concentrated hydrochloric acid, the solution boiled, diluted, and treated with strips of platinum and pure zinc; a black stain on the platinum = *antimony*. The zinc is dissolved in hydrochloric acid and mercuric chloride added; a white precipitate (Hg_2Cl_2) becoming grey $(Hg) = tin$.

In the separation of arsenic, antimony, and tin by ammonium carbonate, this solvent dissolves an appreciable amount of stannic sulphide, which is reprecipitated by acids as a white oxysulphide (Schmidt, Ber. 1894, 27, 2739).

Boiling the mixed sulphides with concentrated hydrochloric acid effects a separation by dissolving the tin and antimony compounds, leaving nearly the whole of the arsenious sulphide undissolved. The mixed sulphides may also be dissolved in aqueous sodium peroxide, which produces sodium arsenate, antimonate, and stannate. On boiling this solution with excess of ammonium chloride, hydrated stannic oxide is precipitated (*v.* J. Walker, Chem. Soc. Trans. 1903, 83. 184; *cf.* Caven, Chem. Soc. Proc. 1910, 26. 176).

(B) The precipitate insoluble in ammonium sulphide is boiled with nitric acid (1 vol. acid sp.gr. 1·20 : 2 vols. H_2O), the residue dissolved in aqua regia, excess of acid expelled, and stannous chloride added; a white precipitate (Hg_2Cl_2) indicates *mercury*. The nitric acid solution is evaporated to a small bulk with sulphuric acid, diluted with cold water and filtered; white residue $(PbSO_4)$ indicates *lead*. The filtrate is rendered ammoniacal, blue colour = *copper*; white precipitate $(Bi(HO)_3) = bismuth$, confirmed by dissolving in hydrochloric acid and diluting considerably with water (BiOCl). The colour of the filtrate discharged by potassium cyanide (excess); the solution saturated with hydrogen sulphide, a yellow precipitate (CdS) = *cadmium* (confirmation is essential, since a yellow cyanogen derivative may be precipitated at this stage).

GROUP III. (phosphates absent).—The mixed hydroxides, suspended in water, are warmed with excess of sodium peroxide and filtered. A residue $(Fe_2O_3 \cdot xH_2O$, which may contain some $MnO_2)$ indicates *iron*. The filtrate is divided into two parts, (i.) boiled with excess of ammonium chloride, white gelatinous precipitate $(Al(OH)_3)$ = *aluminium*; (ii.) acidified with dilute acetic acid and lead acetate added, yellow precipitate $(PbCrO_4) = chromium$.

GROUP III. (phosphates present).—If the original solution was acid, this group precipitate may contain phosphates insoluble in neutral or alkaline solutions. The sodium peroxide separation is applied to one-third of the precipitate; the remainder is dissolved in dilute hydrochloric acid, the solution nearly neutralised with pure sodium carbonate, and treated successively with ammonium acetate, acetic acid, and ferric chloride until no further precipitate is produced and the solution is deep red. The mixture is boiled and filtered hot; the filtrate is then examined for the metals of Groups IV. and V., and for magnesium. The precipitate, which is neglected, contains ferric phosphate and basic ferric acetate. Ammonium formate may be used instead of acetate in this separation (Tower, J. Amer. Chem. Soc. 1910, 32, 953).

The phosphoric acid may also be removed by evaporating the filtrate from Group II. to dryness with nitric acid and granulated tin, when an insoluble residue is obtained consisting of metastannic and phosphostannic acids.

GROUP IV.—The mixed sulphides, washed with hydrogen sulphide water, are dissolved in aqua regia, or hydrochloric acid and potassium chlorate. Excess of sodium hydroxide is added to the solution after expelling excess of acid; the precipitate collected, and the filtrate treated with hydrogen sulphide: white precipitate (ZnS) = *zinc*. The precipitated hydroxides are dissolved in hydrochloric acid, excess of ammonium acetate added, and the solution saturated with sulphide. Any black precipitate is removed and the filtrate rendered ammoniacal; pink precipitate (MnS) = *manganese*.

The black precipitate is tested in the borax bead; a brownish-yellow colour indicates *nickel* present and cobalt absent. If the bead is blue (= *cobalt*), the precipitate is dissolved in hydrochloric acid, potassium chlorate added, excess of acid expelled, and the solution *nearly* neutralised with sodium carbonate; excess of potassium cyanide is then added, and the solution boiled in an open dish. An excess of sodium hypochlorite or freshly prepared sodium hypobromite is added to the warm solution; a black precipitate $(Ni_2O_3 \cdot xH_2O) = nickel$; the filtrate contains potassium cobalticyanide $(K_3Co(CN)_6)$.

A quicker separation of the Group IV. sulphides may be effected by digesting them with cold dilute hydrochloric acid (1 : 20). This treatment should bring the zinc and manganese into solution, leaving the sulphides of nickel and cobalt undissolved; but it is generally found that appreciable quantities of the latter metals are present in the filtrate. Alternative methods of detecting and separating nickel and cobalt are given under special reactions.

GROUP V.—Dissolve the washed precipitate in dilute acetic acid, add aqueous potassium chromate; yellow precipitate $(BaCrO_4) = barium$: filtrate boiled with concentrated aqueous ammonium sulphate; white precipitate $(SrSO_4) = strontium$: final filtrate treated with ammonium oxalate; white precipitate $(CaC_2O_4 \cdot xH_2O) = calcium$. Owing to their close relationship, a sharp separation of the three metals is extremely difficult. The following alternative process has recently been worked out (*v.* Bray, J. Amer. Chem. Soc. 1909, 31, 611).

The group precipitate, which may contain magnesium, is dissolved in 20 c.c. of 30 p.c. acetic acid, solution neutralised with ammonia, 3 c.c. of acetic acid added, diluted to 40 c.c., 10 c.c. of 20 p.c. potassium chromate slowly added, solution boiled for 2 minutes; yellow precipitate $(BaCrO_4)$. Three c.c. of ammonia added to filtrate, diluted to 60 c.c., 50 c.c. of alcohol (95 p.c.) added; after 10 minutes yellow precipitate $(SrCrO_4)$. Without washing this precipitate, 200 c.c. of water are added to filtrate, the solution boiled, and 40 c.c. of 4 p.c. ammonium oxalate added; after 10 minutes white precipitate (CaC_2O_4). *Magnesium* is precipitated in filtrate as a colourless crystalline precipitate $(Mg(NH_4)PO_4 \cdot 6H_2O)$ by adding ammonia and sodium phosphate.

GROUP VI.—A portion of the filtrate from V. examined for *magnesium* (*v. supra*), the remainder evaporated to dryness and ignited to expel ammonium salts. The residue dissolved in a small bulk of water, the solution filtered if necessary, examined by flame test and divided into two parts, (i.) platinic chloride added; yellow crystalline precipitate (K_2PtCl_6) = *potassium*; (ii.) potassium pyroantimonate added; colourless crystalline precipitate ($Na_2H_2Sb_2O_7,6H_2O$) = *sodium*.

GROUP SEPARATION IN THE PRESENCE OF THE RARER METALS.

In the presence of the less commonly occurring elements, the ordinary group separations require, in certain instances, to be modified very considerably. A systematic attempt to deal with this problem has recently been made by A. A. Noyes and his collaborators, to whose original memoirs reference should be made for the exact working details of the necessarily somewhat complicated separations, an outline of which is given below (J. Amer. Chem. Soc. 1907, 29, 137; 1908, 30, 481; 1909, 31, 611).

It will be seen that the greater number of the rarer elements are precipitated by the reagents of Groups II., III., and IV. of the foregoing analytical classification; but in the scheme devised by Noyes, Groups III. and IV. are merged into one, and it is chiefly in this comprehensive group that the additional complications are to be found.

GROUP I.—The precipitate may contain *thallous chloride* and *tungstic acid*. The former is extracted by hot water, any lead separated as sulphate, when the filtrate treated with potassium iodide gives a yellow precipitate (TlI) = *thallium*. The hydrated tungstic acid, precipitated by hydrochloric acid from alkali tungstates, remains in the residue, and may be separated from lead and silver by fusion with sodium carbonate. The aqueous solution of alkali tungstate is boiled with zinc and hydrochloric acid, when the development of a blue colouration = *tungsten*.

GROUP II.—Selenium, tellurium, molybdenum, gold, platinum and its allies, are precipitated by hydrogen sulphide in acid solution. Extraction of the group precipitate with yellow ammonium sulphide carries the greater part of these elements into the tin sub-group, but the separation is not quite sharp, for small but appreciable quantities of molybdenum, gold and the platinum metals remain in the insoluble sulphides of the copper sub-group.

A. *Copper sub-group.*—The precipitate boiled with dilute nitric acid (1 vol. of sp.gr. 1·20 : 2 vols. water) partially dissolves; the solution contains lead, copper, cadmium, and bismuth, while the residue contains mercury, gold, platinum, and a trace of tin. The insoluble portion is oxidised with bromine water, potassium chloride and hydrochloric acid are added and the solution concentrated; a yellow crystalline precipitate (K_2PtCl_6) = *platinum*. The excess of acid is expelled from the solution, which is then rendered alkaline and boiled with excess of oxalic acid; a brownish-black precipitate = *gold*.

B. *Tin sub-group.*—The sulphides are reprecipitated by dilute acid from their solution in ammonium sulphide, and digested for 10 minutes with nearly boiling hydrochloric acid (sp.gr. 1·20); the solution contains tin and antimony, and the residue arsenic and the rarer elements. The residue is dissolved by strong hydrochloric acid and potassium chlorate; the solution concentrated to the crystallising point yields a yellow precipitate (K_2PtCl_6) = *platinum*. The filtrate, treated successively with ammonia and magnesia mixture ($MgCl_2,2NH_4Cl$ with $NH_4 \cdot OH$), yields a colourless crystalline precipitate ($Mg(NH_4)AsO_4,6H_2O$) = *arsenic*. The filtrate from the double arsenate is evaporated to remove ammonia, and then boiled with oxalic acid, and the brownish-black precipitate (*gold*) extracted with hydrochloric acid to dissolve any co-precipitated tellurous acid. The filtrate from the gold is concentrated and acidified with strong hydrochloric acid, and after removing any precipitated potassium chloride, sodium sulphite (in *slight* excess) is added when a red precipitate = *selenium*. The filtrate from selenium is diluted and treated successively with potassium iodide and solid sodium sulphite (excess); the double iodide, K_2TeI_6, becomes reduced, and a black precipitate = *tellurium*. The final filtrate is boiled with hydrochloric acid to expel sulphur dioxide, and to the cooled solution 10 p.c. potassium thiocyanate and stannous chloride (or a scrap of zinc) are successively added, when a red colouration ($Mo(CNS)_4$) soluble in ether = *molybdenum*.

GROUPS III. and IV.—The filtrate from Group II. is boiled to expel hydrogen sulphide, treated with moderately strong ammonia, the colour of the precipitate being noted, and the ammoniacal mixture heated nearly to boiling and treated with ammonium sulphide, or preferably, in the presence of nickel, with hydrogen sulphide to saturation. In the presence of vanadium the filtrate has a reddish colour, and on adding hydrochloric acid brown vanadium sulphide is precipitated. The acid filtrate is boiled to expel hydrogen sulphide, and treated with ferric chloride and ammonia to precipitate last traces of vanadium. The presence of this metal in the sulphide and ferric hydroxide precipitates is confirmed by dissolving in nitric acid (sp.gr. 1·20), diluting and adding hydrogen peroxide, when an orange-yellow colouration = *vanadium*.

The group precipitate is dissolved in hydrochloric acid (sp.gr. 1·12), adding, if necessary, some nitric acid or bromine water. The solution is then boiled with hydrochloric acid to remove nitric acid, and treated in a platinum dish with 40 p.c. hydrofluoric acid, and evaporated to dryness. An insoluble residue indicates the fluorides of the rare earth metals (thorium, cerium, yttrium, erbium, &c.); the aqueous extract, which contains all the other metals of this analytical group, is evaporated successively with hydrochloric and nitric acids. The insoluble fluorides are decomposed by hot sulphuric acid, and the resulting sulphates of the rare earth metals subjected to special tests for these elements.

The nitric acid solution of the other metals of the group is treated successively with caustic soda solution, dry sodium peroxide, and aqueous sodium carbonate, when a precipitate B and a filtrate A are obtained. This treatment

separates these metals into two sub-groups, and the method is valid even when phosphates are present.

A. *The aluminium sub-group* (may contain sodium glucinate, zincate, aluminate, vanadate, chromate, and peruranate). The solution is acidified with nitric acid (sp.gr. 1·42) and diluted considerably, solid sodium hydrogen carbonate added in moderate excess and the mixture heated in a stoppered bottle. The precipitate (containing zinc, glucinum, and aluminium) is dissolved in hydrochloric acid, and the solution rendered ammoniacal; the zinc remains in solution, while the hydroxides of glucinum and aluminium are precipitated. These hydroxides are dissolved in strong hydrochloric acid, ether (1·5 vols.) is added, and the cooled solution saturated with hydrogen chloride, white crystalline precipitate $(AlCl_3,6H_2O) = aluminium$. The ethereal filtrate is evaporated, treated with ammonia, any precipitate dissolved in 10 p.c. sodium hydrogen carbonate, the solution saturated with hydrogen sulphide ; the filtrate from any precipitated sulphide is acidified, boiled, and rendered ammoniacal, when a white flocculent precipitate $(Gl(OH)_3) = glucinum$.

The filtrate obtained from the first treatment with sodium hydrogen carbonate is acidified with nitric acid, and just neutralised with caustic soda : 2 c.c. of nitric acid (sp.gr. 1·20) and 20 c.c. of 20 p.c. lead nitrate are added ; yellow precipitate = *chromium*. The lead is removed with hydrogen sulphide, the excess of gas boiled off, vanadyl salts oxidised to vanadates with bromine, any excess of this reagent being removed by boiling. The solution, after neutralisation with ammonia, is treated successively with 5 c.c. of 30 p.c. acetic acid, 2 grams of ammonium sulphate (or nitrate), and 2 grams of sodium phosphate ; the mixture is heated to boiling, when a white precipitate $(UO_2(NH_4)PO_4) = uranium$. The final filtrate is rendered ammoniacal, saturated with hydrogen sulphide, acidified with acetic acid, and boiled ; dark precipitate = *vanadium*.

B. *The iron-manganese sub-group* (may contain the hydroxides and phosphates of iron, manganese, cobalt, nickel, zinc (traces), titanium, and zirconium, together with calcium, strontium, barium, and magnesium, as carbonates and phosphates). The precipitated hydroxides, &c., are dissolved in hydrochloric acid, the solution evaporated down with strong nitric acid, and treated with 0·5 gram of solid potassium chlorate ; brown precipitate = *manganese*. A portion of the filtrate tested for phosphoric acid, when, if present, the remainder is treated with ammonium hydroxide till nearly alkaline, and boiled with ferric chloride and ammonium acetate. The filtrate contains the ordinary metals of Groups III. and IV., together with magnesium ; the precipitate consists of the hydroxides, phosphates, and basic acetates of iron, zirconium, titanium, and possibly thallium (tervalent). This precipitate is dissolved in hydrochloric acid (sp.gr. 1·12), and the solution shaken with an equal volume of ether. The ethereal extract contains ferric and thallic chlorides ; the hydrochloric acid solution the zirconium and titanium. The latter is evaporated down with sulphuric acid until the hydrogen chloride is expelled, the residue taken up with

water and treated with hydrogen peroxide and subsequently with sodium phosphate ; orange-yellow colouration $(TiO_3) = titanium$; white flocculent precipitate $(Zr(OH)\cdot PO_4) = zirconium$. The final filtrate is reduced with sulphurous acid, when a white flocculent precipitate $(Ti(OH)\cdot PO_4)$ confirms *titanium*.

GROUPS V. and VI.—In the presence of lithium it is preferable to precipitate magnesium in the calcium group. The filtrate from Groups III. and IV. is concentrated to 10 c.c. and treated with 30 c.c. of 20 p.c. ammonium carbonate and 30 c.c. of 95 p.c. alcohol. After 30 minutes the precipitation is complete, the magnesium being present as the double carbonate $(MgCO_3, (NH_4)_2CO_3,4H_2O)$. The treatment of the group precipitate has already been described under Group V. (*v. supra*). The filtrate is evaporated to dryness and ignited. The residue is taken up with 10 c.c. of water, and one-third tested for lithium by adding 0·5 c.c. of 10 p.c. caustic soda and 2 c.c. of 10 p.c. sodium phosphate, heating to boiling and adding 1 c.c. of alcohol, white precipitate $(Li_3PO_4) = lithium$. The filtrate from this phosphate is tested for potassium by adding acetic acid and sodium cobaltinitrite. The remaining two-thirds of the solution, containing the alkali metals, are tested for sodium by potassium pyroantimonate after removing the lithium as fluoride by ammonia and ammonium fluoride.

Examination for Acids.

Although it is not possible to separate the acidic radicles into a limited number of groups, each having a group reagent, yet the reactions may be divided into (i.) preliminary tests made on the original solution or substance ; and (ii.) systematic tests made on suitably prepared solutions. The reactions may be conveniently carried out in the following order :—

I. *Preliminary tests* (compare dry reactions).

1. The original substance or solution is warmed with dilute hydrochloric or sulphuric acid. A gas is evolved, carbon dioxide, turning lime-water milky = *carbonate* ; sulphur dioxide = *sulphite* ; hydrogen sulphide, blackening lead acetate paper = *sulphide* (not all) ; nitrous fumes = *nitrite* ; hydrogen cyanide, odour of bitter almonds = *cyanide*.

2. The original substance or solution warmed slowly with strong solution of sodium dichromate slightly acidified, carbon dioxide evolved, confirms *carbonate* in presence of sulphite.

3. *Heating with concentrated sulphuric acid.*— The foregoing gases may be evolved, and in addition the following :—

(a) *Colourless :*

Fuming acid gas etching glass = *fluoride* ; fuming acid gas not etching = *chloride* ; odour of vinegar = *acetate* ; carbon monoxide, blue flame = *formate, ferrocyanide* ; carbon monoxide and dioxide = *oxalate* ; sulphur dioxide and sulphur sublimate = *thiosulphate*.

(b) *Colour.*

Orange vapour, bromine = *bromide* ; violet vapour and hydrogen sulphide = *iodide* ; nitrous fumes = *nitrite, nitrate* ; oxides of carbon and sulphur with charring = *tartrate, citrate, malate* ; yellow explosive chlorine oxide = *chlorate*.

4. *Heating with alcohol and concentrated*

sulphuric acid, green flame = *borate*. Before performing this test chlorates must be decomposed by igniting the original substance, otherwise an explosion may result.

5. *Heating with concentrated sulphuric acid and sand*, a colourless gas (SiF_4), giving a gelatinous precipitate on moist rod, confirms *fluoride*.

II. *Systematic tests.*—Before testing a solution for acids, boil with excess of pure sodium carbonate to remove heavy metals, filter, and carefully neutralise with nitric acid.

1. *Barium chloride* in neutral solution yields: (α) a white precipitate, insoluble in hydrochloric acid = *sulphate*, *silicofluoride*; (β) a white precipitate, soluble in hydrochloric acid = *sulphite*, *carbonate*, *phosphate*, *oxalate*, *borate*, *fluoride*, *silicate*, *tartrate*; (γ) a yellow precipitate = *chromate*.

2. To a portion of the neutral solution add *calcium chloride* in excess, allow to stand for some time with occasional shaking, and filter. A white precipitate (α) insoluble in acetic acid = *oxalate* (*sulphate* in strong solutions); (β) soluble in acetic acid = *phosphate*, *borate*, and other acids precipitated by barium chloride.

Calcium *tartrate* after washing is soluble in potash, and is re-precipitated on diluting and boiling.

The filtrate from the precipitate in the cold is boiled for some time and filtered hot ; a white precipitate = *citrate* (*malate* in strong solutions). The filtrate from this precipitate is allowed to cool and then mixed with excess of alcohol ; a white precipitate = *succinate*, *malate*.

3. *Silver nitrate* in neutral solution yields :

(α) A precipitate soluble in nitric acid.

(1) White = *oxalate*, *borate*, *tartrate*, *benzoate*, &c.

(2) Yellow = *phosphate*, *arsenite.*

(3) Brick-red = *arsenate.*

(4) Dark-red = *chromate.*

(β) A precipitate insoluble in nitric acid.

Soluble in ammonia : White = *chloride (hypochlorite)*, *cyanide*, *thiocyanate* ; yellowish-white = *bromide* ; orange-red = *ferricyanide* ; white = *ferrocyanide* (sparingly soluble).

Insoluble in ammonia : Yellow = *iodide* ; black = *sulphide*.

4. *Ferric chloride* in neutral solutions yields :

(α) A colouration : blood-red = *acetate*, *formate* (precipitate on boiling), *thiocyanate* (no precipitate on boiling) ; violet = *salicylate*, *thiosulphate* (fugitive) ; bluish-black = *tannate*, *gallate* ; greenish-brown = *ferricyanide* (dark-blue precipitate on adding stannous chloride).

(β) A precipitate : buff = *benzoate*, *carbonate* ; reddish-brown = *succinate* ; white = *phosphate* ; black = *sulphide* ; bluish- or greenish-black = *tannate*, *gallate.*

Sulphur acids. (1) Detect *sulphate* by barium chloride, and *sulphide* by lead acetate, &c. Make part of the solution slightly alkaline with potash, add zinc sulphate in considerable excess, and filter. Test one part of the filtrate for *thiosulphate* by means of hydrochloric acid ; to the other part add acetic acid till *faintly* acid, sodium nitroprusside in small quantity, and potassium ferrocyanide ; a pink precipitate indicates a *sulphite*.

(2) Separation of soluble sulphates, sulphites, sulphides, and thiosulphates in neutral solution.

Precipitate *sulphide* as CdS, PbS, or ZnS by adding cadmium carbonate or lead carbonate sludge or zinc chloride solution. Add strontium nitrate and leave for 12 hours ; the precipitated strontium *sulphate* and *sulphite* separated by hydrochloric acid, the filtrate contains the *thiosulphate*, decomposed by strong hydrochloric acid, giving sulphur and sulphur dioxide (Autenrieth and Windaus, Zeitsch. anal. Chem. 1898, 37, 295).

Chloride, bromide, and iodide. (1) Place the substance in a small flask connected with a small bulb U-tube containing a little starch paste and placed in a beaker of water. Add water and ferric sulphate solution to the substance in the flask, and heat to boiling. If iodine is present, the starch paste becomes blue. Remove the cork, boil with fresh additions of ferric sulphate till all iodine is expelled. Now add a few crystals of potassium permanganate, connect with a bulb tube containing chloroform, and again boil. If bromine is present, the chloroform is coloured brown. Boil with addition of more permanganate until all bromine is expelled, filter and test filtrate for chlorine (Hart, Amer. Chem. J. 1884, 6, 346).

(2) After iodine has been detected by means of nitrogen oxides in sulphuric acid, evaporate part of the solution to dryness with sodium carbonate, fuse with ten times its weight of potassium dichromate till all iodine is expelled, place in a small dry retort, and heat with strong sulphuric acid. Part of the distillate is agitated with water and carbon disulphide ; if bromine is present, the latter becomes orange-red. The remainder of the distillate is neutralised with ammonia, and tested for chromic acid by acidifying with acetic acid and adding lead acetate. The presence of chromic acid indicates the presence of chlorine in the original substance.

(3) A neutral solution of the three halides is treated with potassium iodate and dilute acetic acid ; as iodine is liberated, more iodate is added and the solution boiled until all the iodine is eliminated. The solution is mixed with half its volume of 5N-nitric acid, bromine is evolved and the solution boiled till colourless. A little potassium iodide added to destroy the iodate in excess, and the solution boiled till colourless, then an equal volume of strong nitric acid and a few drops of silver nitrate are added, when a white precipitate indicates a chloride: The strong nitric acid holds in solution any trace of silver iodate. If thiocyanic acid is present, the test for iodine must be made in a small portion of the original solution, adding sodium acetate as well as acetic acid to depress the dissociation of the latter (Benedikt and Snell, J. Amer. Chem. Soc. 1903, 25, 809).

Other acids must be detected by special tests. Iodine, and ferrocyanides and ferricyanides must be removed before testing for nitrates.

To remove iodine, ferrocyanic, ferricyanic, and thiocyanic acids, add excess of a mixture of cupric and ferrous sulphates, and filter. To remove excess of copper and iron (which is not always necessary) heat to boiling, add slight excess of *pure* caustic potash or soda, and filter.

To remove bromine and iodine, acidify with dilute sulphuric acid, and boil with successive additions of potassium permanganate until the liquid has a faint permanent pink tinge ; filter.

To remove hypochlorous and nitrous acids, acidify with dilute sulphuric acid, and boil. Nitrous acid can also be decomposed by boiling with a strong solution of ammonium chloride.

For an alternative classification of the acidic radicles into analytical groups, compare T. Milobendski (J. Russ. Phys. Chem. Soc. 1909, 41, 1301).

SPECIAL REACTIONS.

In the following lists only the most charac teristic and useful reactions have been given ; negative reactions, and others not particularly characteristic, have, as a rule, been omitted (*see also* Dry reactions).

METALS.

The metals are arranged in the order of their occurrence in the systematic separation.

Silver.

Hydrochloric acid, a white precipitate (AgCl), insoluble in hot water and in nitric acid ; soluble in ammonia and reprecipitated by nitric acid in excess. *Potassium chromate,* a dark-red pre cipitate (Ag_2CrO_4); soluble in mineral acids and decomposed by caustic alkalis. *Potassium cyanide,* white precipitate (AgCN) soluble in excess to $KAg(CN)_2$.

Lead.

Hydrochloric acid, a white precipitate ($PbCl_2$), soluble in hot water, from which it crystallises on cooling ; insoluble in ammonia. *Hydrogen sulphide,* a black precipitate (PbS), insoluble in ammonium sulphide (in presence of hydrogen halides, intermediate red compounds are pro duced, *e.g.* $PbS,4PbI_2$, J. Amer. Chem. Soc. 1895, 17, 511 ; 1901, 23, 680); soluble in nitric acid. *Sulphuric acid,* a white precipitate ($PbSO_4$), soluble in hot hydrochloric acid ; in soluble in dilute sulphuric acid ; soluble in ammonium acetate (Noyes and Whitcomb, J. Amer. Chem. Soc. 1905, 27, 747). *Potassium chromate,* yellow precipitate ($PbCrO_4$), in soluble in acetic acid ; soluble in potassium hydroxide.

Thallium.

Hydrochloric acid, white precipitate (TlCl), only slightly soluble in hot water. *Potassium iodide,* pale-yellow precipitate (TlI), even in dilute solution. *Sulphuric acid,* no precipitate (diff. from Pb). *Sodium cobaltinitrite* gives red crystalline precipitate $(Tl_3Co(NO_2)_6)$ (J. Russ. Phys. Chem. Soc. 1910, 42, 94).

Tungsten.

Hydrochloric acid, a yellowish-white pre cipitate (H_2WO_4), insoluble in excess of the dilute acid ; soluble in the concentrated acid and in tartaric acid : fragments of zinc added to this solution produce a blue colouration. *Stannous chloride,* a yellow precipitate, which becomes blue if mixed with hydrochloric acid and heated. *Ammonium sulphide,* no precipitate with sodium tungstate, but on acidifying, light-brown precipitate (WS_3), insoluble in hydrochloric acids, soluble in ammonium sulphide.

Mercury.

Mercurous compounds. Hydrochloric acid, white precipitate (Hg_2Cl_2), insoluble in hot water : insoluble in ammonia, but blackened (NH_2Hg_2Cl). *Stannous chloride,* grey precipi tate (Hg). *Metallic copper,* becomes coated with mercury, which can be sublimed.

Mercuric compounds. Hydrogen sulphide,

white precipitate, becoming yellow, red, and then black (HgS) ; insoluble in ammonium sulphide ; appreciably soluble in alkali sulphides ($Hg(SNa)_2$), insoluble in nitric acid ; soluble in aqua regia. *Stannous chloride,* white precipitate (Hg_2Cl_2), becoming grey (Hg) with excess of the reagent. *Potassium iodide,* scarlet precipitate (HgI_2), soluble in excess. *Metallic copper,* as mercurous salts.

Bismuth.

Hydrogen sulphide, brown precipitate (Bi_2S_3), insoluble in ammonium sulphide ; soluble in nitric acid. *Ammonia,* white precipitate ($Bi(HO)_3$), soluble in hydrochloric acid. *Water* in large excess (with previous addition of am monium chloride if chlorides are absent), white precipitate (BiOCl), soluble in hydrochloric acid ; insoluble in tartaric acid. *Reducing agents* (sodium stannite, hypophosphites, hydrosulphites, formaldehyde in alkaline solution) reduce bis muth compounds to elemental bismuth.

Copper.

Hydrogen sulphide, black precipitate (CuS), insoluble in ammonium sulphide and in dilute sulphuric acid ; soluble in nitric acid and in potassium cyanide. *Ammonia,* blue precipitate, soluble in excess to dark-blue solution. *Potas sium ferrocyanide,* chocolate-brown precipitate, insoluble in dilute acids ; in very dilute solutions colouration only ; decomposed by sodium hydroxide, yielding blue copper hydroxide.

Cadmium.

Hydrogen sulphide, yellow precipitate (CdS), insoluble in ammonium sulphide and potassium cyanide ; soluble in nitric acid and hot dilute sulphuric acid. *Ammonia,* white precipitate (CdH_2O_2), readily soluble in excess. *Caustic potash* or *soda,* white precipitate (CdH_2O_2) insoluble in excess.

Tin.

Stannous compounds. Hydrogen sul phide, dark-brown precipitate (SnS), soluble in yellow but not in colourless ammonium sul phide. *Mercuric chloride,* white precipitate (Hg_2Cl_2), becoming grey (Hg).

Stannic compounds. Hydrogen sulphide, yellow precipitate (SnS_2), soluble in ammonium sulphide ; appreciably soluble in ammonium carbonate (Ber. 1894, 27, 2739); soluble in concentrated hydrochloric acid; dissolves in aqueous caustic soda. *Stannic chloride,* boiled with copper becomes stannous chloride. When *zinc* and *platinum* are placed in the solution, no black stain on the platinum ; crystals of tin on the zinc.

Antimony.

Hydrogen sulphide, orange precipitate (Sb_2S_3), soluble in ammonium sulphide and in concen trated hydrochloric acid ; insoluble in ammo nium carbonate. *Water* in excess (with ammo nium chloride if chlorides are absent), white precipitate (SbOCl), soluble in hydrochloric acid and in tartaric acid. *Zinc* and *platinum,* a black stain on the platinum (Sb), soluble in nitric acid and in ammonium sulphide.

Arsenic.

Hydrogen sulphide, yellow precipitate, soluble in ammonium sulphide and in ammonium car bonate ; insoluble in concentrated hydrochloric acid. *Metallic copper,* boiled with the liquid after acidifying with hydrochloric acid, is covered with a shining grey deposit (As_2Cu_5), which, when

heated in a tube, yields a sublimate of arsenious oxide (Reinsch's test) (Clark, Chem. Soc. Trans. 1893, 63, 884, 886). *Nascent hydrogen* produced from zinc and dilute sulphuric acid reduces arsenic compounds to volatile arsine (AsH_3), which decomposes on gently heating, giving an arsenic deposit soluble in aqueous hypochlorites. Antimony compounds under these conditions also give a black deposit (antimony), insoluble in hypochlorites (Marsh's test). Zinc and caustic soda reduce arsenic compounds, liberating arsine, which produces a yellow-to-brown stain on mercuric chloride paper (Gutzeit's test, Chem. Soc. Trans. 1901, 79, 715).

Arsenites. *Ammonio-silver nitrate,* yellow precipitate (Ag_3AsO_3), soluble in nitric acid and ammonia. *Ammonio-cupric sulphate,* bright-green precipitate ($CuHAsO_3$), turns red by boiling with caustic soda.

Arsenates. *Ammonio-silver nitrate,* brick-red precipitate (Ag_3AsO_4), soluble in nitric acid and ammonia. *Ammonium chloride, ammonia,* and *magnesium sulphate,* white crystalline precipitate (NH_4MgAsO_4). *Ammonio-cupric sulphate,* pale-blue precipitate, turned black by boiling with caustic soda.

When arsenic acid or arsenates are present, they should be reduced by heating with sulphurous acid or ammonium iodide or hydriodic acid (Bull. Soc. chim. Belg. 1909, 23, 88) before applying hydrogen sulphide or Reinsch's test (Usher and Travers, Chem. Soc. Trans. 1905, 87, 1370).

Platinum.

Hydrogen sulphide, brown precipitate (PtS_2) on heating, soluble in ammonium sulphide. *Ammonium chloride* or *potassium chloride,* yellow crystalline precipitate (M_2PtCl_6), less soluble in presence of alcohol. *Potassium iodide,* in dilute solution red colouration (K_2PtI_6), very delicate test. *Stannous chloride,* in dilute solution, brownish-red colouration, delicate test.

Palladium.

Hydrogen sulphide, black precipitate (PdS), insoluble in ammonium sulphide; soluble in hot hydrochloric acid and in aqua regia. *Potassium iodide,* black precipitate (PdI_2), somewhat soluble in excess. *Mercuric cyanide,* yellowish white, gelatinous precipitate ($PdCy_2$), readily soluble in ammonia. *Ammonium chloride,* no precipitate (diff. from Pt); on addition of chlorine water, orange precipitate (($NH_4)_2PdCl_6$). *Potassium chloride,* precipitate ($2KCl \cdot PdCl_2$) only in very concentrated solutions.

Iridium.

Hydrogen sulphide, decolourisation followed by brown precipitate (Ir_2S_3), soluble in ammonium sulphide. *Caustic potash,* a greenish colouration which, on heating with exposure to air, changes slowly to azure blue (diff. from Pt). *Ammonium chloride* or *potassium chloride,* dark-brown or red precipitate (double chloride), insoluble in a saturated solution of the precipitant. Both salts become olive green with potassium nitrite and other reducing agents, especially in hot solutions. *Strong sulphuric acid* and *ammonium nitrate,* on heating, blue colouration.

Osmium.

Hydrogen sulphide, in acid but not in neutral solution, black precipitate (OsS_4), insoluble in ammonium sulphide. *Nitric acid* on boiling oxidises osmium compounds to osmic tetroxide (OsO_4), characteristic odour and yellow solution in caustic soda.

Ruthenium.

Hydrogen sulphide, blue solution followed by brown precipitate of ruthenium sulphide. *Sodium thiosulphate* in ammoniacal solution to dilute solutions of ruthenium, a purplish-red colouration. *Zinc* reduces $RuCl_3$, giving a blue solution and then precipitating ruthenium.

Rhodium.

Hydrogen sulphide, on warming, black precipitate (Rh_2S_3), insoluble in ammonium sulphide; soluble in boiling nitric acid. *Potassium nitrite,* warmed with sodium rhodium chloride, gives orange-yellow precipitate ($K_3Rh(NO_2)_6$).

Gold.

Hydrogen sulphide, black precipitate (Au_2S_3) in cold, brown precipitate (Au_2S) in hot, solution; soluble in yellow ammonium sulphide. *Oxalic acid* or *ferrous sulphate,* brown or purple precipitate, yellow and lustrous when rubbed. *Stannous* and *stannic chlorides,* purplish precipitate, insoluble in hydrochloric acid. *Hydrogen peroxide,* in very dilute alkaline solution, liberates finely divided gold having a beautiful blue shimmer.

Molybdenum.

Hydrogen sulphide, brownish-black precipitate (MoS_3) on heating, soluble in ammonium sulphide. *Sodium phosphate,* in presence of nitric acid, yellow precipitate on heating, soluble in ammonia and in excess of the alkaline phosphate. *Potassium thiocyanate* and zinc or stannous chloride, red colouration due to $Mo(CNS)_4$, soluble in ether. *Concentrated sulphuric acid,* when strongly heated with molybdenum compounds, develops a deep-blue colouration. *Phenylhydrazine,* in 50 p.c. acetic acid, red colouration (Ber. 1903, 36, 512).

Selenium.

Hydrogen sulphide, yellow precipitate, becoming dark on heating, soluble in ammonium sulphide. *Sulphurous acid,* in presence of hydrochloric acid, a red precipitate, which becomes grey on heating, and is soluble in potassium cyanide. *Stannous chloride* and other reducing agents behave in a similar manner. *Barium chloride,* (i.) white precipitate ($BaSeO_3$), soluble in dilute hydrochloric acid ; (ii.) white precipitate ($BaSeO_4$), insoluble in dilute hydrochloric acid; soluble in the strong acid, evolving chlorine. *Concentrated sulphuric acid,* green colouration.

Tellurium.

Hydrogen sulphide, brown precipitate (TeS_2) at once from tellurites, but from tellurates only after boiling with hydrochloric acid. *Potassium iodide,* to tellurite in acid solution, black precipitate (TeI_4). *Reducing agents* ($SnCl_2$,Zn), black precipitate (Te). *Concentrated sulphuric acid,* carmine colouration.

Aluminium.

Ammonia, white gelatinous precipitate (AlH_3O_3), insoluble in excess and in ammonium carbonate ; soluble in acids. *Caustic potash* or *soda,* white gelatinous precipitate (AlH_3O_3), soluble in excess ; reprecipitated on adding ammonium chloride and heating.

Chromium.

Chromic salts. *Ammonia,* greenish or purplish precipitate (CrH_3O_3), soluble in acids ; insoluble in ammonium carbonate. *Caustic*

potash or *soda*, green precipitate (CrH_5O_3), soluble in excess, but reprecipitated on boiling.

Chromates. Hydrogen sulphide in acid solution, reduction to chromic salt with change of colour to green. *Lead acetate*, bright yellow precipitate ($PbCrO_4$), insoluble in acetic acid. *Silver nitrate*, dark-red precipitate (Ag_2CrO_4), soluble in nitric acid.

Iron.

Ferrous salts. Ammonium sulphide, black precipitate (FeS), soluble in acids. *Ammonia* or *caustic potash* or *soda*, white precipitate, rapidly becoming green and then brown. *Potassium ferrocyanide*, white precipitate, gradually becoming dark blue. *Potassium ferricyanide*, dark-blue precipitate ($Fe_3(FeCy_6)_2$). *Potassium thiocyanate*, no reaction.

Ferric salts. Ammonium sulphide, black precipitate ($2FeS + S$, or Fe_2S_3), soluble in acids. *Ammonia* or *caustic potash* or *soda*, reddish-brown precipitate (FeH_3O_3), soluble in acids. *Potassium ferrocyanide*, dark-blue precipitate ($Fe_4(FeCy_6)_3$), insoluble in dilute acids. *Potassium ferricyanide*, no precipitate; greenish-brown colouration. *Potassium thiocyanate*, blood-red colouration; not affected by boiling or by hydrochloric acid.

Thorium.

Ammonia, caustic soda, or *potash*, white gelatinous precipitate ($Th(OH)_4$), insoluble in excess. *Ammonium* or *sodium carbonate*, white precipitate, basic carbonate; soluble in excess. *Oxalic acid*, white precipitate ($Th(C_2O_4)_2,2H_2O$), insoluble in excess and insoluble in mineral acids, but soluble in ammonium oxalate. *Potassium fluoride* or *hydrofluoric acid*, white precipitate (ThF_4). *Potassium sulphate*, white crystalline precipitate ($2K_2SO_4,Th(SO_4)_2,2H_2O$).

Cerium.

Ammonia, white precipitate of basic salt, insoluble in excess. *Caustic potash* or *soda*, white precipitate ($Ce(OH)_3$), insoluble in excess; becomes yellow when exposed to air. *Oxalic acid*, white precipitate ($Ce_2(C_2O_4)_3$), insoluble in excess, but soluble in a large quantity of hydrochloric acid. *Potassium sulphate*, white precipitate even in somewhat acid solutions ($CeK_3(SO_4)_3$), insoluble in a saturated solution of potassium sulphate. *Hydrogen peroxide*, in ammoniacal solution, orange-brown precipitate.

Glucinum.

Ammonia, white precipitate (GlH_2O_2), insoluble in excess. *Caustic potash* or *soda*, the same precipitate, soluble in excess, but reprecipitated on boiling (diff. from Al). *Ammonium carbonate*, white precipitate, easily soluble in excess (diff. from Al).

Glacial acetic acid dissolves $Gl(OH)_2$ or $GlCO_3$, and the residue, after evaporating to dryness, is the basic acetate ($Gl_4O(CH_3 \cdot CO_2)_6$), readily soluble in chloroform, ether, acetone, the alcohols, and other organic media; it melts at 283°–284°, and can be sublimed without decomposition. *Sodium hydrogen carbonate*, 10 p.c. dissolves $Gl(OH)_2$; dilution to 1 p.c. causes reprecipitation.

Uranium.

Ammonia, caustic potash, or *soda*, yellow precipitate, insoluble in excess, but readily soluble in ammonium carbonate. *Ammonium sulphide*, brown precipitate, readily soluble in ammonium carbonate. *Potassium ferrocyanide*, chocolate-brown precipitate, readily decomposed by alkalis, yielding yellow alkali diuranates.

Titanium.

Ammonia, caustic potash, or *soda*, or *ammonium sulphide*, white precipitate (H_2TiO_3), insoluble in excess; soluble in dilute sulphuric and hydrochloric acids. *Potassium ferrocyanide*, dark-brown precipitate. *Sodium thiosulphate*, complete precipitation on boiling. *Hydrogen peroxide*, to a slightly acid solution of titanium sulphate; orange-red colouration; weakened by fluorides. *Reducing agents* ($SnCl_2$ or Zn and HCl) produce a violet colouration ($TiCl_3$). *Catechol* added to dilute solutions of titanic or titanous salts, yellowish-orange colouration, very delicate test, but interfered with by mineral acids or alkalis (Ber. 1909, 42, 4341).

Zirconium.

Ammonia, ammonium sulphide, caustic soda, white gelatinous precipitate, dissolving in dilute acid, but less readily after boiling; precipitation prevented by tartaric acid. *Oxalic acid*, white precipitate ($Zr(C_2O_4)_2$), readily soluble in ammonium oxalate or in excess of oxalic acid. *Hydrogen peroxide*, white milky precipitate (Zr_2O_5), evolving chlorine when boiled with hydrochloric acid. *Turmeric paper*, moistened with acid solution of zirconium salt, becomes reddish-brown on drying.

Zinc.

Ammonium sulphide, white precipitate (ZnS), soluble in dilute hydrochloric acid; insoluble in acetic acid and in alkalis. *Caustic potash* or *soda*, white precipitate (ZnH_2O_2), soluble in excess. *Potassium ferrocyanide*, white precipitate, insoluble in dilute hydrochloric acid (Zn_2FeCy_6).

Manganese.

Ammonium sulphide, pink precipitate (MnS), soluble in dilute hydrochloric acid and in acetic acid. *Caustic potash* or *soda*, white precipitate (MnH_2O_2), insoluble in excess, becoming brown on exposure to air. Boiled with dilute *nitric acid* and *lead peroxide* (in absence of chlorine), a purplish crimson solution of permanganic acid.

Nickel.

Ammonium sulphide, black precipitate (NiS), somewhat soluble in excess; insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Caustic potash* or *soda*, pale-green precipitate (NiH_2O_2), insoluble in excess. *Potassium cyanide*, precipitate ($NiCy_2$), soluble in excess, forming $NiCy_2,2KCy$, which is not altered when boiled with exposure to air. This solution, heated with excess of sodium hypochlorite solution, or mixed with bromine in the cold, yields a precipitate of black nickelic hydroxide (NiH_3O_3). *Dimethylglyoxime* ($CH_3 \cdot C(NOH) \cdot C(NOH) \cdot CH_3$) (Tschugaeff, Ber. 1905, 38, 2520), added to ammoniacal or acetic acid solution of nickel salts, scarlet precipitate (distinction from cobalt). *Dicyanodiamidine* (H. Grossmann and W. Heilborn, Ber. 1908, 41, 1878) added to ammoniacal solutions of cobalt and nickel salts containing excess of sucrose, yellow crystalline precipitate ($Ni(N_4H_5C_2O)_2,2H_2O$), the presence of cobalt indicated by the reddish-violet colour of the solution.

Cobalt.

Ammonium sulphide, black precipitate (CoS), insoluble in cold dilute hydrochloric acid; soluble in strong acids. *Caustic potash*, pale-blue

precipitate (CoH_2O_2), slightly soluble in excess, forming a blue solution. *Potassium cyanide,* precipitate ($CoCy_2$), soluble in excess, forming $CoCy_2,4KCy$, and when this solution is boiled with exposure to air it is changed to K_3CoCy_6, which is not precipitated by sodium hypochlorite or bromine. *Potassium nitrite* to dilute acetic acid solutions, yellow crystalline precipitate ($K_3Co(NO_2)_6$). *Nitroso-β-naphthol* $NO·C_{10}H_6·OH$ (Ilinski and Knorre, Ber. 18, 699) dissolved in dilute acetic acid added to feebly acid solutions of cobalt and nickel, brick-red precipitate ($Co(NO·C_{10}H_6·O)_3$); solution examined for nickel (Chaplin, J. Amer. Chem. Soc. 1907, 29, 1029).

Vanadium.

Ammonium sulphide, dark-brown solution, which when acidified yields a brown precipitate (V_2S_4). *Ammonium chloride,* white precipitate of ammonium meta-vanadate (NH_4VO_3). *Potassium ferrocyanide,* in acid solution, a green precipitate. If a solution of an alkaline vanadate is agitated with *hydrogen peroxide* and *ether,* the solution acquires a deep purplish-red colour, but the ether remains colourless. *Mild reducing agents* (SO_2, H_2S, HBr, alcohol, &c.) reduce vanadates in acid solutions to blue divanadyl salts. *Strong reducing agents* (zinc and aluminium with acids) produce a series of colour changes—blue, green, and violet.

Columbium.

Hydrogen fluoride and *potassium fluoride* produce potassium columbo-fluoride, which when boiled in aqueous solution yields potassium columbium oxyfluoride (K_2CbOF_5,H_2O) (solubility 1 in 12·5 cold water). *Mineral acids,* partial precipitation of columbic acid from alkali columbates : *zinc* and *acid,* blue colouration, turning brown ; *potassium ferrocyanide,* greyish-green precipitate.

Tantalum.

Hydrogen fluoride and *potassium fluoride* produce potassium tantalofluoride (K_2TaF_7) (solubility 1 in 154 cold water), separating in colourless needles. *Mineral acids,* white precipitate of tantalic acid. *Potassium ferrocyanide,* reddish-brown precipitate (*v.* Weiss and Landecker, Zeitsch. anorg. Chem. 1909, 64, 65).

Calcium.

Ammonium carbonate, white precipitate ($CaCO_3$), soluble in acids. *Sulphuric acid,* white precipitate only in very concentrated solutions. *Ammonium oxalate,* white precipitate (CaC_2O_4), insoluble in acetic and oxalic acids, but soluble in hydrochloric acid.

Strontium.

Ammonium carbonate, white precipitate, soluble in acids ($SrCO_3$). *Ammonium sulphate,* white precipitate, especially on boiling. *Ammonium oxalate,* white precipitate (SrC_2O_4), soluble in hydrochloric acid ; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate,* white precipitate ($SrSO_4$), forming slowly.

Barium.

Ammonium carbonate, white precipitate ($BaCO_3$), soluble in acids. *Ammonium oxalate,* white precipitate (BaC_2O_4), soluble in hydrochloric acid ; insoluble in acetic acid. *Sulphuric acid* or *calcium sulphate,* an immediate white precipitate, insoluble in acids and alkalis. *Potassium chromate,* yellow precipitate ($BaCrO_4$), insoluble in acetic acid.

Magnesium.

Sodium phosphate, in presence of ammonia and ammonium chloride, white precipitate, rapidly becoming crystalline ($NH_4MgPO_46H_2O$). Forms slowly in dilute solutions, formation being accelerated by agitation and by rubbing the sides of the beaker with a glass rod ; soluble in acids.

Potassium.

Chloroplatinic acid H_2PtCl_6, yellow crystalline precipitate (K_2PtCl_6), somewhat soluble in water; insoluble in alcohol. *Sodium hydrogen tartrate,* in neutral or feebly acid solutions, a white crystalline precipitate ($KHC_4H_4O_6$), forming slowly in dilute solutions. If the solution contains free mineral acids, nearly neutralise with soda and add sodium acetate.

Sodium cobaltinitrite in acetic acid solution, yellow precipitate ($K_2NaCo(NO_2)_6$). *Sodium 1-amino-β-naphthol-6-sulphonate* (eikonogen) in 5-10 p.c. solutions, crystalline precipitate ($KSO_3·C_{10}H_5(NH_2)·OH$) ; negative results with ammonium and magnesium salts (Alvarez, Chem. Soc. Abstr. 1905, ii. 355).

Ammonium.

Ammonium salts are readily volatile. *Heated with lime, caustic potash,* or *soda,* ammonia gas is given off, and is recognised by its smell and its action on test paper.

Chloroplatinic acid, yellow crystalline precipitate (($NH_4)_2PtCl_6$), slightly soluble in water; insoluble in alcohol. *Sodium hydrogen tartrate,* white crystalline precipitate ($NH_4HC_4H_4O_6$), forming slowly in dilute solutions.

Nessler's reagent (K_2HgI_4 and KOH), brownish-red precipitate or colouration (NHg_2I,H_2O), very delicate test.

Sodium.

Flame colouration, intense yellow.

Although all sodium salts are more or less soluble, some dissolve only sparingly, *e.g.* sodium oxalate and sodium α-naphthylamine-8-sulphonate.

Potassium pyroantimonate, white crystalline precipitate ($Na_2H_2Sb_2O_7·6H_2O$) (J. Amer. Chem. Soc. 1909, 31, 634) ; from neutral or slightly alkaline solutions.

Dihydroxytartaric acid, colourless precipitate ($CO_2Na.C(OH)_2·C(OH)_2·CO_2Na$) (Fenton, Chem. Soc. Trans. 1895, 67, 48). *Solution of bismuth nitrate in 50 p.c. potassium nitrite containing cæsium nitrite,* yellow crystalline precipitate ($5Bi(NO_2)_3,9CsNO_2,6NaNO_2$); very delicate test, not interfered with by lithium and metals of alkaline earths (Ball, Chem. Soc. Trans. 1909, 95, 2126). Sodium chloride, obtained by slow evaporation of a solution acidified with hydrochloric acid, crystallises in distinct cubes.

Lithium.

Chloroplatinic acid, no precipitate.

Sodium phosphate, in alkaline solution ; white precipitate (Li_3PO_4), soluble in hydrochloric acid, not reprecipitated by ammonia except on boiling. Lithium chloride is soluble in ethyl or amyl alcohol, and in pyridine. *Ammonium hydrogen fluoride,* white precipitate (LiF).

Cæsium.

Flame colouration, violet.

Chloroplatinic acid, yellow crystalline precipitate (Cs_2PtCl_6), insoluble in boiling water. *Tartaric acid,* crystalline precipitate, somewhat soluble in water. *Stannic chloride,* white

precipitate (Cs_2SnCl_6). *Lead chloride dissolved in chlorine water*, yellow precipitate (Cs_2PbCl_6). Cæsium carbonate is soluble in alcohol (diff. from K, Rb).

Rubidium.

Flame colouration, violet.

Chloroplatinic acid, yellow crystalline precipitate (Rb_2PtCl_6), insoluble in boiling water. *Tartaric acid*, white crystalline precipitate, less soluble than the cæsium compound (Reactions of Cs and Rb, *v.* Wells, Amer. J. Sci. [3] **43**, 17 and 46, 186, and 265).

ACID RADICLES.

The acid radicles are arranged partly in the order of the systematic separation and partly with a view to bring together those acids which are commonly associated or which resemble one another in their reactions. In all cases, unless otherwise specified, it is important that the solution should be neutral.

Sulphates.

Barium chloride, white precipitate ($BaSO_4$), insoluble in acids and alkalis.

Sulphites.

Hydrochloric acid, sulphur dioxide evolved, but no sulphur precipitated. *Barium chloride*, white precipitate ($BaSO_3$), soluble in hydrochloric acid. *Iodine solution*, sulphites are converted into sulphates. Neutralise, then *slightly* acidify with acetic acid ; add excess of *zinc sulphate*, a small quantity of *sodium nitroprusside* and *potassium ferrocyanide.* The precipitate of zinc ferrocyanide has a pink colour.

Strontium chloride, white precipitate ($SrSO_3$), different from thiosulphate SrS_2O_3, being much more soluble.

Hyposulphites ('hydrosulphites,' *e.g.* $Na_2S_2O_4$, $2H_2O$) owe their technical application to their reducing action on indigotin and its sulphonic acids—the colour is discharged (indigo-white). *Silver nitrate*, black precipitate (Ag). *Mercuric chloride*, black precipitate (Hg). *Copper sulphate*, reddish precipitate (Cu and Cu_2H_2), in very dilute solution, colloidal copper.

Thiosulphates.

Hydrochloric acid, sulphur dioxide evolved and sulphur precipitated. *Silver nitrate*, white precipitate ($Ag_2S_2O_3$), rapidly changing to black (Ag_2S), soluble in excess of alkaline thiosulphate, forming a much more stable solution. With *sodium nitroprusside*, *zinc sulphate*, and *potassium ferrocyanide*, the precipitate is white. *Iodine solution* converts soluble thiosulphates into tetrathionates, which give no precipitate with barium chloride. *Ferric chloride*, transient violet colouration ($Fe_2(S_2O_3)_3$).

Persulphates ($e.g.$ $K_2S_2O_8$).

The dry salts evolve oxygen on heating. *Barium chloride*, no precipitate in the cold, on warming oxygen evolved and $BaSO_4$ precipitated. *Silver nitrate*, black precipitate (silver peroxide). *Other metallic salts* (Pb, Mn, Co, and Ni) yield their hydrated peroxides.

Monopersulphuric acid (*Caro's acid*) $HO·SO_2·O·OH$, produced by adding a persulphate to cold concentrated sulphuric acid, and pouring the mixture on to ice. *Aromatic amines (e.g.* p-$Cl·C_6H_4·NH_2$) give coloured oxidation products with persulphates and nitroso- compounds (*e.g.* $Cl·C_6H_4·NO$) with Caro's acid.

Thionic acids (*v.* Chem. Soc. Trans. 1880, 608).

Sulphides.

Hydrochloric acid, in most cases evolution of hydrogen sulphide, especially on heating. *Lead nitrate* or *acetate*, black precipitate (PbS). *Silver nitrate*, black precipitate (Ag_2S), insoluble in ammonia, sodium thiosulphate, and potassium cyanide. *Sodium nitroprusside*, in alkaline solutions an intense but somewhat fugitive violet colouration.

Phosphates.

Barium chloride, white precipitate $Ba_3(PO_4)_2$, soluble in dilute acids. *Calcium chloride*, white precipitate ($Ca_3(PO_4)_2$), soluble in acetic acid. *Silver nitrate*, yellow precipitate (Ag_3PO_4), soluble in nitric acid and in ammonia. *Pyrophosphates* and *metaphosphates* give white precipitates of their silver salts with silver nitrate, but metaphosphates alone, unlike ortho- and pyro-phosphates, coagulate albumin. *Magnesium sulphate*, in presence of ammonium chloride and ammonia, white crystalline precipitate ($NH_4MgPO_4 6H_2O$), soluble in acids. *Ammonium molybdate*, in nitric acid solution, on heating. a yellow precipitate (($NH_4)_3PO_4·12MoO_3$) soluble in ammonia, and soluble in excess of an alkaline phosphate.

Phosphites.

Barium chloride, white precipitate ($BaHPO_3$), soluble in hydrochloric acid. *Silver nitrate*, precipitate of metallic silver, especially in presence of ammonia, and on heating. *Mercuric chloride*, white precipitate (Hg_2Cl_2), becoming grey (Hg). Heated with *nitric acid*, phosphites are converted into phosphates. Heated alone, phosphites evolve phosphine. *Copper sulphate*, pale blue precipitate.

Hypophosphites.

Heated alone, evolve phosphine. *Barium chloride*, white precipitate only in strong solution ($Ba(H_2PO_2)_2$). *Silver nitrate*, metallic silver precipitated. *Copper sulphate*, brown precipitate, cuprous hydride (Cu_2H_2).

Carbonates.

Hydrochloric acid, effervescence, with evolution of carbonic anhydride, which turns lime water turbid. *Barium chloride*, white precipitate ($BaCO_3$), soluble in acids with effervescence. *Mercuric chloride*, red precipitate (basic carbonate); bicarbonates give only a yellowish opalescence. *Calcium sulphate*, white precipitate, immediately with carbonate, but only after standing with bicarbonate (Leys, J. Pharm. Chim. 1897, (vi.) **6**, 441).

Borates.

Barium chloride, white precipitate in not too dilute solutions, soluble in acids. *Silver nitrate*, in strong solution, white precipitate ($AgBO_2$); in dilute solution, dark-grey deposit (Ag_2O).

Mix the solid substance with concentrated sulphuric acid in a small crucible, add alcohol, and ignite ; the alcohol flame is green, especially at the edges. Mix the solid substance with three parts potassium hydrogen sulphate and one part powdered fluorspar, and heat on platinum wire in the cold area of the flame ; a bright-green colouration (due to BF_3) is observed. *Turmeric paper*, moistened with acid solution of boric acid, becomes reddish brown on drying.

Silicates.

Solutions of silicates heated with acids, ammonium chloride, or ammonium carbonate, deposit silicic acid. Dilute solutions must be

evaporated to dryness, and on treating the residue with dilute hydrochloric acid insoluble silica is left.

Most silicates are insoluble in water; some are decomposed by acids; others are only decomposed by fusion with about four times their weight of a mixture of equal parts of sodium and potassium carbonates.

Silicofluorides.

Concentrated sulphuric acid, in leaden or platinum capsule, hydrogen fluoride and silicon fluoride are evolved. *Barium chloride,* colourless crystalline precipitate $BaSiF_6$. Silicofluorides on heating evolve silicon fluoride, leaving residues of metallic fluorides.

Oxalates.

Barium chloride or *calcium chloride,* white precipitate, insoluble in acetic acid, but soluble in hydrochloric acid.

Acidify with sulphuric acid, and add potassium permanganate; the colour of the latter is rapidly and completely discharged.

Heat the solid substance with concentrated sulphuric acid; carbonic anhydride and carbonic oxide are evolved. The latter burns with a blue flame.

Fluorides.

Barium chloride, white precipitate (BaF_2), soluble in hydrochloric acid. *Silver nitrate,* no precipitate with soluble fluorides. *Concentrated sulphuric acid,* especially when heated, produces hydrogen fluoride, which attacks glass. The substance and acid are placed in a small leaden or platinum crucible, which is covered with a watch-glass protected by a thin coating of wax, part of which has been scratched away so as to

Chlorides.

Silver nitrate, a white precipitate (AgCl), insoluble in nitric acid, soluble in ammonia; darkens when exposed to light. *Manganese dioxide* and *sulphuric acid,* evolution of chlorine on heating. *Potassium dichromate* and *strong sulphuric acid,* evolution of chromyl chloride on heating. This forms with ammonia a yellow solution of ammonium chromate.

Bromides.

Silver nitrate, yellowish white precipitate (AgBr), insoluble in nitric acid; moderately soluble in ammonia; readily soluble in potassium cyanide or sodium thiosulphate. *Manganese dioxide* and *sulphuric acid,* orange vapours of bromine, which turn starch paste orange. *Chlorine water* liberates bromine, which dissolves in ether or carbon bisulphite, forming an orange-brown solution. Bromides heated with *potassium dichromate* and *strong sulphuric acid* yield bromine, which forms a colourless solution with ammonia.

Iodides.

Silver nitrate, yellow precipitate (AgI), insoluble in nitric acid or ammonia; soluble in potassium cyanide or sodium thiosulphate. *Manganese dioxide* and *sulphuric acid* yield violet vapours of iodine, which colour starch paste blue. *Chlorine water, bromine water,* or *potassium dichromate in presence of hydrochloric acid,* liberates iodine, which turns starch paste an intense blue. The colour disappears on heating, and reappears on cooling. The liberated iodine may be agitated with carbon bisulphide or chloroform, when it yields a violet solution. *Nitro-*

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gen oxides sulphuric acid likewise liberate iodine, but do not liberate bromine unless added in large excess.

Cyanides.

Silver nitrate, white precipitate (AgCN), insoluble in nitric acid, but soluble in ammonia, sodium thiosulphate, or excess of the alkaline cyanide.

Add ferric chloride and ferrous sulphate; make alkaline with caustic potash or soda, and then acidify with hydrochloric acid. A dark blue precipitate of Prussian blue is formed.

Evaporate the solution with an excess of yellow ammonium sulphide to complete dryness on a water-bath; dissolve in very dilute hydrochloric acid, and add ferric chloride; a blood-red colouration is produced.

Most cyanides evolve hydrocyanic acid, recognisable by the smell, when treated with hydrochloric or sulphuric acid.

Mercuric cyanide cannot be recognised by these tests. It yields cyanogen when heated in a closed tube, and is decomposed when heated with strong sulphuric acid.

Ferrocyanides.

Silver nitrate, white precipitate (Ag_4FeCy_6), insoluble in nitric acid and sparingly soluble in ammonia; soluble in potassium cyanide. *Ferric chloride,* dark-blue precipitate ($Fe_4(FeCy_6)_3$). *Ferrous sulphate,* white precipitate, rapidly becoming blue. *Copper sulphate,* chocolate-brown precipitate (Cu_2FeCy_6), or in very dilute solution a brown colouration.

Ferricyanides.

Silver nitrate, orange precipitate (Ag_3FeCy_6), soluble in ammonia; insoluble in nitric acid. *Ferrous sulphate,* dark-blue precipitate ($Fe_3(FeCy_6)_2$), insoluble in dilute acids; decomposed by alkalis. *Ferric chloride,* a greenish-brown colouration.

Thiocyanates.

Silver nitrate, white precipitate (AgCNS), soluble in ammonia; insoluble in nitric acid. *Ferric chloride,* blood-red colouration, not affected by boiling nor by hydrochloric acid; decolourised by mercuric chloride. *Copper sulphate,* a black precipitate changing to white ($Cu_2(CNS)_2$) on standing or addition of a reducing agent. *Moderately strong sulphuric acid* evolves carbon oxysulphide, which burns to carbon dioxide and sulphur dioxide. *Cobalt chloride* and the solution shaken up with ether and amyl alcohol, azure-blue colouration ($K_2Co(CNS)_4$).

Cyanates.

Cobalt chloride, in aqueous alcoholic solution, blue soluble double salt ($K_2Co(CNO)_4$), decomposed by excess of water.

Nitrates.

Sulphuric acid evolves nitric acid on heating; if metallic copper is added, red-brown nitrogen oxides are given off.

The neutral solution is mixed with ferrous sulphate, and concentrated sulphuric acid is poured down the side of the tube so as to form a layer at the bottom; a dark-brown ring is formed at the junction of the two liquids. Iodine and bromine must be removed before applying this test, and the liquid must be cold. Nitrate in presence of nitrite: destroy nitrite by boiling acetic acid solution with urea or hydrazine sulphate; then add potassium iodide, starch, and a fragment of zinc; blue colouration denotes nitrate.

Nitrites.

Silver nitrate, a white precipitate in concentrated solutions.

Mix the solution with potassium iodide and starch and acidify with acetic acid ; a deep-blue colouration is produced, owing to the liberation of iodine. Nitrites heated with dilute acids evolve nitrogen oxides. *Metaphenylenediamine hydrochloride*, Bismarck brown colouration.

A dilute solution of *α-napthylamine* and *sulphanilic acid* acidified with acetic acid ; a red colouration of azo- compound (*cf.* Zeitsch. angew. Chem. 1900, 235).

Hypochlorites.

Silver nitrate, a white precipitate of silver chloride. *Lead nitrate*, a white precipitate becoming orange-red, finally brown. *Manganous salts*, a brown precipitate (MnO_2, xH_2O). *Indigo solution*, decolourised even in an alkaline solution.

Chlorates.

Warm a small quantity of the solid with concentrated sulphuric acid ; a yellow explosive gas is produced with detonations.

Acidify the solution with sulphuric acid, add indigo solution, and then sulphurous acid or a sulphite drop by drop ; the colour of the indigo is discharged.

Perchlorates.

Concentrated sulphuric acid, no explosive gas. *Titanous sulphate*, perchlorates reduced to chlorides.

Bromates.

Silver nitrate, white precipitate, $AgBrO_3$, decomposed by hot hydrochloric acid with evolution of bromine. *Barium chloride*, white precipitate, $Ba(BrO_3)_2$. *Sulphurous acid*, bromine liberated.

Iodates.

Silver nitrate, white curdy precipitate ($AgIO_3$), soluble in ammonia ; reduced to yellow silver iodide by sulphurous acid. *Barium chloride*, white precipitate ($Ba(IO_3)_2$). *Sulphurous acid*, iodine liberated.

Periodates.

Silver nitrate, yellowish-white, red, or brown precipitate depending on the acidity of the periodate solution. *Barium chloride*, white precipitate. *Manganous sulphate*, red precipitate Mn_2HIO_6, turning brown. *Reducing agents* (H_2SO_3, $Ti_2(SO_4)_3$, Zn, etc.) convert periodates readily into iodides. *Mercuric nitrate*, orange-red precipitate $5HgO,I_2O_7$, different from iodates, which give white $Hg(IO_3)_2$.

Tartrates.

Calcium chloride, in excess, a white precipitate ($CaC_4H_4O_6$), soluble in acids and in potash solution. Complete precipitation requires time, and is promoted by vigorous agitation. *Potassium acetate*, in presence of free acetic acid, a white crystalline precipitate ($KHC_4H_4O_6$), forming slowly in dilute solutions. *Silver nitrate*, a white precipitate, soluble in nitric acid or ammonia. If the washed precipitate is dissolved in the least possible quantity of dilute ammonia, and the solution heated, the test-tube is coated with a mirror of metallic silver. *Ferrous sulphate*, followed by few drops of hydrogen peroxide and excess of caustic soda, bluish-violet colouration.

Citrates.

Calcium chloride, or *lime water*, in excess in neutral solution, a white precipitate ($Ca_3(C_6H_5O_7)_2$) only on boiling. *Potassium salts*, no precipitate. *Cadmium chloride*, gelatinous white precipitate ($Cd(C_6H_5O_7)_2$), insoluble in hot water ; soluble in acetic acid (diff. from tartrates). *Mercuric sulphate* (5 p.c.), following by potassium permanganate, white turbidity, mercuric acetone-dicarboxylate (halogens should be absent) (Denigès).
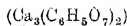
Malates.

Calcium chloride, no precipitate even on boiling, except in strong solutions ; precipitate in dilute solutions on adding alcohol. *Lime water*, no precipitate even on boiling. *Silver nitrate*, white precipitate ($Ag_2C_4H_4O_5$), which becomes grey on boiling. *Lead acetate*, white precipitate ($PbC_4H_4O_5$), which when washed melts in boiling water.

Succinates.

Barium chloride, or *calcium chloride*, no precipitate except after addition of alcohol. *Ferric chloride*, reddish-brown precipitate ($Fe_2(C_4H_4O_4)_3$), soluble in acids ; decomposed by ammonia.

Benzoates.

Hydrochloric acid, white crystalline precipitate of benzoic acid, slightly soluble in water. *Ferric chloride*, a buff precipitate $Fe_2(C_7H_5O_2)_3$, soluble in hydrochloric acid with liberation of benzoic acid ; decomposed by ammonia. *Concentrated sulphuric acid* and *alcohol* on heating produce ethyl benzoate, distinctive odour. *Soda lime* : benzoates heated with this reagent are decomposed, evolving benzene.

Salicylates.

Ferric chloride, intense purple colour : not affected by glycerol ; interfered with by alkalis, dilute mineral acids, tartaric, citric, and oxalic acids, and certain other substances such as borax, sodium phosphate, ammonium and sodium acetates. *Silver nitrate*, white precipitate in neutral solutions. *Bromine water*, white precipitate, which with sodium amalgam yields phenol. *Concentrated sulphuric acid* and *methyl alcohol* on heating give methyl salicylate ('oil of winter-green'). *Diazotised aniline* or *sulphanilic acid* gives an orange azo- compound.

Acetates.

Ferric chloride, a dark-red colouration, discharged on boiling, with precipitation of a basic ferric acetate. Also discharged by hydrochloric acid. Heated with *strong sulphuric acid*, acetic acid is evolved. If alcohol is added, ethyl acetate is formed and is recognised by the smell.

Formates.

Silver nitrate, a white precipitate in concentrated solutions ; the solution or precipitate rapidly becomes black (Ag), especially on heating. *Ferric chloride*, a red colour, discharged on boiling, with precipitation of basic ferric formate ; also discharged by hydrochloric acid.

A solid formate mixed with concentrated sulphuric acid gives off carbonic oxide even in the cold, but no carbonic anhydride.

Gallic acid.

Ferric chloride, in neutral solutions, a bluish-black precipitate or colouration. *Gelatin* or *albumin*, no precipitate. *Potassium cyanide*, red colouration, which disappears on standing, but reappears on agitation in presence of air. *Caustic soda*, green colouration gradually

darkening, and with excess becoming brownish-red. *Lime water*, bluish-grey precipitate.

Tannic acid.

Ferric chloride, bluish-green or bluish-black precipitate or colouration. *Gelatin* or *albumin*, yellowish-white precipitate. *Potassium cyanide*, no colouration. *Caustic soda*, reddish-brown colouration gradually darkening. *Lime water*, grey precipitate.

Phenol.

Ferric chloride, violet colouration, destroyed by acids. *Bromine water*, white precipitate (tribromophenol and tribromophenol bromide). *Concentrated sulphuric acid* and a fragment of *sodium nitrite*, on gently warming, greenish blue solution, turned red when poured into water, and changed again to blue by caustic alkali.

Pyrogallol.

Silver nitrate or *Fehling's solution*, readily reduced: *Caustic alkalis*, brown solutions, rapidly darkening owing to absorption of oxygen. *Formaldehyde* and *strong hydrochloric acid*, white precipitate becoming red, and finally purple.

Uric acid.

Alkali urates reduce *silver nitrate*, and when heated with solid caustic soda, ammonia is evolved, and an alkali cyanide is produced. *Nitric acid*: evaporate solution to dryness on water-bath, reddish colouration, rendered violet by ammonia, and turned blue by caustic soda (Murexide test).

QUANTITATIVE ANALYSIS.

GRAVIMETRIC METHODS.

A few metals are separated and weighed in the metallic condition, but the majority of metallic and acidic radicles are weighed in the form of one or other of their compounds. In order that a compound may be available for the determination of one of its constituents, it should be of perfectly definite composition and not highly hygroscopic or otherwise liable to alter; it must be insoluble in the liquid in which it is formed, and insoluble in an excess of the reagent; it must be easily freed from impurities, and capable of being brought into the proper condition for weighing without tedious and complicated operations. It is also desirable that the compound should contain only a small proportion of the constituent to be estimated, since the effect of the unavoidable error of experiment is thus minimised. An estimation of chlorine in the form of silver chloride is more accurate than an estimation of silver in the same way, since only one-fourth of the error of experiment represents chlorine, whilst three-fourths represent silver.

A description will first be given of a few typical gravimetric methods; then an alphabetical list of metals and acid radicles, with a summary of methods available in each case; followed by a series of methods of separation of general applicability. Special methods for the analysis of technical products will be found in the articles dealing with these materials.

GENERAL METHODS OF ESTIMATION.

I. *As Sulphides.*

(a) *With previous precipitation by hydrogen sulphide.* The solution should be moderately dilute and distinctly acidified with HCl, but any large quantity of this acid must be avoided. Nitric acid and nitrates, which should be absent

as far as possible, may be removed by repeated evaporation with strong hydrochloric acid, but this treatment is not admissible if the metals present form volatile chlorides; if present, a much higher degree of dilution is necessary. In most cases precipitation is accelerated and the precipitate rendered more granular by keeping the liquid warm. A current of washed hydrogen sulphide is passed through the solution until it is thoroughly saturated, and the flask is closed and left in a warm place until the precipitate has settled. Molybdenum and the metals of the platinum group are only completely precipitated after prolonged treatment with the gas. The precipitate is protected from air as far as possible during filtration, and the liquid used for washing should contain hydrogen sulphide in order to prevent oxidation.

When arsenic is present, the liquid should be heated with pure sulphurous acid to reduce arsenic acid, and the excess of sulphurous acid expelled before treatment with hydrogen sulphide. In presence of antimony, tartaric acid should be added to prevent co-precipitation of basic antimony chloride.

When copper is precipitated as sulphide in presence of zinc, the copper sulphide should be washed once or twice with dilute hydrochloric acid of sp.gr. 1·05 containing hydrogen sulphide, and then with water also containing the gas.

(β) *With previous precipitation by ammonium sulphide.* Add to the warm solution a considerable quantity of ammonium chloride, which is found to promote precipitation and render the precipitate more granular, then ammonia to alkaline reaction, and a slight excess of ammonium sulphide. Close the flask and allow to stand in a warm place until the precipitate has settled. Protect from air as far as possible during filtration, and wash with water containing ammonium chloride and a little ammonium sulphide or hydrogen sulphide.

The precipitated sulphide is treated in one of two ways: it is collected on a weighed filter, dried at a definite temperature and weighed; or heated with sulphur in a current of hydrogen, and then weighed.

In the first case it is essential to ensure the absence of co-precipitated sulphur, and for this purpose the dried precipitate is treated with pure carbon bisulphide and again dried, or, in the case of cadmium, mercury, or bismuth, the moist precipitate is treated with a warm concentrated solution of sodium sulphite, again washed, and dried.

When the sulphide is stable at a moderately high temperature and is not reduced by hydrogen, Rose's method is employed. The dry precipitate is separated from the filter, which is then burnt, and the precipitate and filter ash are introduced into a porcelain crucible and mixed with pure finely powdered sulphur. The crucible is provided with a perforated lid, through which passes a porcelain tube connected with a hydrogen apparatus. A current of purified and dried hydrogen is passed into the crucible, which is gradually heated to full redness until excess of sulphur is expelled, allowed to cool in a current of hydrogen, and weighed.

Non-volatile sulphides may be collected in a wide Soxhlet tube and dried *in situ* over a ring burner at 300°, while a current of pure dry

carbon dioxide is conducted through the tube. This treatment removes both moisture and co-precipitated sulphur (Cahen and Morgan, Analyst, 1909, 34, 3).

II. *As Oxide.*

(*a*) *With previous precipitation as hydroxide.* The solution is mixed with ammonium chloride, heated to boiling, and ammonia added in slight excess. A large excess of ammonia will partially redissolve some of the precipitate, and must be expelled by boiling. The precipitate is washed with hot water.

If ammonia is inadmissible, pure caustic potash or soda is used as the precipitant. Excess of alkali must be avoided, and the precipitate must be very thoroughly washed, since small quantities of alkali are somewhat firmly retained.

In both cases it is better to precipitate in a porcelain or platinum vessel than in glass.

Non-volatile carbon compounds, such as sugar, glycerol, alkaline, tartrates, and citrates, &c., more or less completely prevent precipitation of hydroxides by ammonia or caustic potash, or soda, and hence must first be removed by calcination. Moderately strong nitric acid attacks filter paper, forming soluble products, which prevent the precipitation of metallic hydroxides.

(*β*) *With previous precipitation as carbonate.* The solution is nearly neutralised, heated to boiling, and mixed with a slight excess of sodium carbonate, boiling being continued until all carbon dioxide is expelled. The precipitate is washed with hot water. Ammonium carbonate can be used in some cases, and has the advantage of not introducing a fixed alkali. In these cases the precipitate should be washed with water containing a little ammonia and ammonium carbonate.

The precipitated hydroxide or carbonate is placed in a crucible (with previous separation from the filter paper if the metal is easily reducible), and is gradually heated to full redness, care being taken that no reducing gases from the flame enter the crucible. Oxides of reducible metals must be heated in a porcelain crucible, but in other cases a platinum crucible may be used with advantage. If carbonates (or oxalates) are being converted into oxides, it is important to secure a circulation of air in order to remove carbon monoxide and carbon dioxide as fast as they are given off, and thus accelerate decomposition. This is done by inclining the crucible and placing the lid across the mouth in a slanting position.

III. *As reduced Metals.*

(*a*) In some cases the metal is precipitated as oxide, which is then dried and heated in hydrogen as in Rose's method for sulphides, the reduced metal being cooled in hydrogen and weighed. This method is especially valuable when, as in the case of cobalt, the oxide obstinately retains small quantities of alkali, which, however, can readily be removed from the reduced metal by washing with water.

(*β*) The other method is to mix the oxide, carbonate, &c., with five or six times its weight of ordinary potassium cyanide, and heat in a capacious porcelain crucible, at first cautiously and afterwards to complete fusion. When reduction is complete, the crucible is allowed to cool, and is tapped occasionally to promote the collection of the reduced metal in a single button.

The cyanide is removed by treatment with water, the metal washed, dried, and weighed. Care should be taken that the metallic button does not contain small fragments of porcelain resulting from the corrosion of the crucible.

IV. *As Sulphate.*

Barium, strontium, and lead are precipitated from solutions in the ordinary way, but other metals are converted into sulphate by treatment with the strong acid, the method being only available when a single metal is present in combination with a volatile acid. The highly concentrated solution, or better, the solid substance, is mixed cautiously with concentrated sulphuric acid in a platinum crucible and then gently heated to expel excess of acid, the crucible being inclined and the lid placed in a slanting position across its mouth. A large excess of acid should be avoided, and care must be taken that the temperature is sufficient to expel the excess of free acid but not sufficient to decompose the sulphate. Sulphates of the alkalis and alkaline earths may be heated to redness. Bismuth sulphate and zinc sulphate decompose if heated above $400°$; magnesium sulphate is not decomposed at $450°$, nor barium or lead sulphate at $500°$ (G. H. Bailey). A temperature of about $350°$ is required to expel the last traces of free sulphuric acid. With lead or bismuth sulphate a porcelain vessel must be used.

GRAVIMETRIC DETERMINATION OF METALS AND ACID RADICLES.

Details of operations will be found under *General Methods of Estimation* (*v.* p. 179), and electrolytic and volumetric methods will be indicated under appropriate headings (*v.* p. 206).

Aluminium.

(*a*) As *oxide*, with previous precipitation with ammonium sulphide, ammonium carbonate, or as basic acetate (*v. Methods of separation*). The aluminium hydroxide is maintained in its insoluble hydrogel form by washing with dilute aqueous ammonium nitrate. The hydroxide may also be precipitated in a form suitable for filtration by boiling the solution of the aluminium salt with potassium iodide and potassium iodate (Stock, Ber. 1900, 33, 548; Compt. rend. 1900, 130, 175).

(*b*) As *phosphate*. The solution is nearly neutralised, mixed with sodium acetate and a small quantity of acetic acid, heated to boiling, sodium phosphate added in excess, and the precipitate washed with hot water, heated, and weighed as aluminium phosphate ($AlPO_4$).

Ammonium.

(*a*) As *platinichloride* $(NH_4)_2PtCl_6$ (*v. Potassium*). The platinic chloride solution should be added before the liquid is heated, and evaporation should not quite be carried to complete dryness.

(*b*) By distillation (*v.* ACIDIMETRY).

Antimony.

(*a*) As *sulphide* Sb_2S_3 (*v.* p. 179). The precipitate is collected (i.) in a weighed Soxhlet tube on an asbestos mat, and dried at $280°$–$300°$ in a current of carbon dioxide (Analyst, 1909, 34, 3); or (ii.) in a Gooch crucible and dried in an air-oven in an atmosphere of carbon dioxide. An aliquot part is then placed in a porcelain boat, and heated in a glass tube in a current of dry carbonic anhydride until it becomes black, and

all admixed sulphur is expelled. The loss of weight is calculated to the whole quantity and deducted from the weight at 100°.

(b) As *oxide* Sb_2O_4, with previous precipitation as sulphide. The sulphide is placed in a porcelain crucible and treated with fuming nitric acid boiling at 86° until completely oxidised, the excess of acid expelled, and the residue heated with partial exposure to air until the weight is constant. The sulphide may also be mixed with 30 to 50 times its weight of precipitated mercuric oxide and heated cautiously until of constant weight. A deep capacious crucible with a lid having a side tube for the exit of vapours has been devised for this and similar estimations.

Arsenic.

(a) As *trisulphide* As_2S_3 (v. p. 179), which is dried at 100°. The dry precipitate should volatilise completely when heated.

(b) As *pentasulphide* As_2S_5. The arsenic is oxidised to arsenic acid by chlorine in alkaline solution, and the precipitation then effected in warm acid solution after decomposing all the chlorate (Brauner and Tomiček, Monatsh. 1887, 8, 642; and Neher, Zeitsch. anal. Chem. 1893, 32, 45).

(c) Arsenic acid is estimated as *magnesium pyroarsenate* $Mg_2As_2O_7$, in the same way as phosphoric acid (*which see*). The filter paper is moistened with a solution of ammonium nitrate and dried before burning, in order to prevent reduction (v. Ducru, Compt. rend. 1900, 131, 886; *cf. also* Friedheim and Michaelis, Zeitsch. anal. Chem. 1895, 34, 505).

Barium.

(a) As *sulphate* $BaSO_4$, by precipitation with sulphuric acid (*v. Sulphuric acid*).

(b) As *carbonate* $BaCO_3$, which may be dried at a temperature below dull redness after moistening the filter ash with ammonium carbonate (*v. General Methods of Estimation*).

(c) As *silicofluoride* (*v. Methods of separation*).

(d) As *bromide* (Thorne, Zeitsch. anal. Chem. 1905, 43, 308).

Glucinum.

As *oxide* GlO, with previous precipitation by ammonia or ammonium sulphide, but not caustic soda or potash, or ammonium carbonate.

Bismuth.

(a) As *oxide* Bi_2O_3, after precipitation with a slight excess of ammonium carbonate. In presence of chlorides or sulphates the precipitate will contain basic chloride or sulphate, and in this (or in any other) case the bismuth may be precipitated as sulphide, which is oxidised in the crucible by fuming nitric acid boiling at 86°, and then heated.

(b) As *sulphide* Bi_2S_3, which is dried at 100° and weighed at intervals of 20–30 minutes. The weight first decreases owing to loss of water, and then increases owing to oxidation; the minimum weight is taken as correct.

(c) As *metallic bismuth* (v. p. 180). Bismuth is precipitated as metal by adding to slightly acid solutions of its salts, formaldehyde and excess of caustic soda, boiling and filtering through a Gooch crucible, the precipitate being washed with alcohol and dried at 105° (Vanino and Treubert, Ber. 1898, 31, 1303).

(d) Other methods: *phosphate* (Stahler and Scharfenberg, Ber. 1905, 38, 3862), *double moly-* *bdate* $Bi(NH_4)$ $(MoO_4)_2$ (Miller and Cruser, J. Amer. Chem. Soc. 1905, 27, 16).

Cadmium.

(a) As *sulphide* CdS, which is dried at 100°, or dissolved in hydrochloric acid, and the solution evaporated to dryness with sulphuric acid, the residue gently ignited and weighed as $CdSO_4$.

(b) As *oxide*, after precipitating as basic carbonate from boiling solutions by potassium (not sodium) carbonate and collecting in a Gooch crucible (Amer. J. Sci. 1906, 20, 456).

Calcium.

(a) As *oxide* CaO, after precipitation with ammonium carbonate or ammonium oxalate (v. Utz, Oest. Chem. Zeit. 1904, 7, 510). In the latter case the solution is made alkaline with ammonia, heated to boiling, and mixed with excess of ammonium oxalate. The precipitate is washed with hot water, and strongly heated until its weight is constant.

(b) As *sulphate* $CaSO_4$, by igniting the carbonate or oxalate with pure sulphuric acid.

Chromium (in chromic salts).

(a) As *oxide* Cr_2O_3, after precipitation by ammonia, or better, ammonium sulphide; or by potassium iodide and iodate (Stock and Massaciu, Ber. 1901, 34, 467).

(b) As *phosphate*, in the same way as aluminium.

Chromium (in chromic acid and chromates).

(a) As *oxide* Cr_2O_3. The solution is neutralised, heated to boiling, and mixed with excess of a neutral solution of mercurous nitrate free from nitrous acid. The precipitate is washed with hot water containing mercurous nitrate, and heated to redness in a porcelain crucible until all mercurial vapours are expelled. The mercurous chromate yields chromic oxide.

(b) As *chromate*, by precipitation with barium chloride in acetic acid solution.

Cobalt.

(a) As *metallic cobalt*, after precipitation as cobaltic hydroxide by caustic soda or potash with bromine (v. p. 180). The solution must be free from ammonium salts, or all ammonia must be expelled by boiling. The precipitate retains traces of alkali, and in accurate estimations the reduced metal should be washed with water, dried, and again heated in hydrogen.

(b) As *sulphate* $CoSO_4$, after precipitation as sulphide, which is treated with nitric acid and then with sulphuric acid (v. p. 180). If the heated sulphate is at all black, it must be treated again with sulphuric acid.

Copper.

(a) As *cuprous sulphide* Cu_2S, using Rose's method, with previous precipitation as cupric sulphide by hydrogen sulphide or sodium thiosulphate (Chem. Zeit. 1895, 19, 1591).

(b) As *oxide*, after precipitation by caustic potash or soda in absence of ammonium salts.

(c) As *cuprous thiocyanate* CuCNS (Rivot Compt. rend. 1854, 38, 868; also Amer. J. Sci. 1902, 13, 20 and 138). The warm solution, which must contain no free nitric acid, is slightly acidified with hydrochloric acid, and mixed gradually with an excess of a moderately strong solution of equal parts of ammonium or potassium thiocyanate and ammonium hydrogen sulphite. When cold, the precipitate is collected in a weighed Gooch crucible, washed with cold water and 20 p.c. alcohol, and dried at 110°–120°.

The precipitate may also be converted into cuprous sulphide by Rose's method. Cuprous thiocyanate is not quite insoluble, especially in presence of much free acid.

Gold.

As *metallic gold.* Nitric acid is removed by evaporation with hydrochloric acid. The solution is acidified with hydrochloric acid, mixed with a large excess of ferrous sulphate solution, and heated gently for a few hours ; or it is acidified with sulphuric acid, mixed with oxalic acid, and allowed to stand in a warm place for several hours. Formaldehyde and hydrogen peroxide in alkaline solution can be used as precipitants (Ber. 1899, 32, 1968). Nitrous acid is also suggested (Jameson, J. Amer. Chem. Soc. 1905, 27, 1444). The precipitate is collected on a weighed filter, washed and dried.

Iron.

(*a*) As *ferric oxide* Fe$_2$O$_3$, after precipitation by ammonia, caustic potash or soda, potassium iodide and iodate (*v. Chromium*), or as basic carbonate, basic acetate or formate. The oxide is heated to redness until its weight is constant ; if heated at a higher temperature, it is partially converted into ferroso-ferric oxide Fe$_3$O$_4$.

(*b*) Ferrous and ferric salts can be separated and estimated gravimetrically by means of barium carbonate and ammonium chloride, when the ferric salt is decomposed, precipitating ferric hydroxide, and the ferrous salt remains in solution.

Lead.

(*a*) As *sulphate* PbSO$_4$. The solution, which should not be dilute, is mixed with dilute sulphuric acid and twice its volume of alcohol, and allowed to stand, and the precipitate washed with alcohol. If the addition of alcohol is inadmissible, the solution is evaporated with a large excess of dilute sulphuric acid, till fumes are evolved. The residue is taken up with cold water and quickly filtered on a Gooch crucible ; and the precipitate is washed with dilute sulphuric acid and afterwards with alcohol to remove all free acid.

(*b*) As *sulphide* PbS, by hydrogen sulphide and Rose's method.

(*c*) As *oxide* PbO, after precipitation by ammonium carbonate, avoiding an excess of ammonium salts.

(*d*) As *metal* (*v.* p. 180).

(*e*) Other methods. As *chromate* and *iodate.*

Magnesium.

(*a*) As *pyrophosphate* Mg$_2$P$_2$O$_7$. The solution is mixed with ammonium chloride in sufficient quantity to prevent precipitation by ammonia, made strongly alkaline with ammonia, and then mixed with excess of sodium phosphate, or, better, ammonium phosphate or microcosmic salt. Care should be taken to avoid rubbing or scratching the sides of the vessel. The liquid is allowed to remain for a few hours, filtered, and the precipitate washed with a mixture of strong ammonia (1 part) and water (5 parts) until the washings give only a faint opalescence with silver nitrate after acidifying with nitric acid. The precipitation of the double phosphate is greatly accelerated and a granular non-adherent product obtained by shaking the mixed solutions in a stoppered cylinder. The precipitate is dried, *cautiously* heated in a platinum crucible until all ammonia is expelled, and then heated

to redness until the weight is constant. If the precipitate is black, owing to partial reduction, it is moistened with a few drops of strong nitric acid, and again heated until perfectly white.

(*b*) As *oxide* MgO, after precipitation as hydroxide by barium hydroxide, or mercuric oxide, or as double carbonate MgCO$_3$(NH$_4$)$_2$CO$_3$ (Zeitsch. anorg. Chem. 1908, 58, 427), the precipitate being strongly ignited (*v.* Zeitsch. anorg. Chem. 1901, 26, 347).

(*c*) As *pyroarsenate* (*v. Pyrophosphate,* and Amer. J. Sci. 1907, 23, 293).

Manganese.

(*a*) As *sulphide* MnS, by Rose's method after precipitation by ammonium sulphide.

(*b*) As *oxide* Mn$_3$O$_4$, after precipitation by sodium carbonate, or ammonium carbonate (Tamm, Zeitsch. anal. Chem. 1872, 11, 425). The hydrated peroxide precipitated by bromine and ammonia, on prolonged ignition yields Mn$_3$O$_4$.

(*c*) As *pyrophosphate* Mn$_2$P$_2$O$_7$. Ammonium chloride and microcosmic salt are added in considerable excess to the cold manganese solution followed by a slight excess of ammonia. The mixture is then heated till the precipitate becomes silky and crystalline. After cooling for 30 minutes, the precipitate is collected on the Gooch, washed with very dilute ammonia, and ignited (Gooch and Austin, Amer. J. Sci. 1898, 6, 150).

(*d*) As *sulphate* (*v.* p. 180, Gooch and Austin, Amer. J. Sci. 1898, 5, 209).

Mercury (in mercurous compounds).

As *mercurous chloride* Hg$_2$Cl$_2$. The dilute cold solution is mixed with a solution of sodium chloride in slight excess, and the precipitate is collected on a weighed filter and dried at 100°.

Mercury (in mercuric compounds).

(*a*) As *sulphide* HgS, which is dried at 100° after precipitation by hydrogen sulphide.

(*b*) As *mercurous chloride* Hg$_2$Cl$_2$. The solution is mixed with excess of hydrochloric acid and phosphorous acid (made by allowing phosphorus to oxidise slowly in moist air), and allowed to remain in a warm place for twelve hours. The precipitate is collected on a weighed filter and dried at 100°.

Molybdenum.

(*a*) As *lead molybdate* PbMoO$_4$. The solution is heated to boiling, mixed with excess of lead acetate, and boiled for a few minutes. The precipitate is washed with hot water, dried at 100°, and heated to low redness in a porcelain crucible.

(*b*) As the *oxide* MoO$_3$. The solution is neutralised with nitric acid, mixed with excess of a neutral solution of mercurous nitrate, the precipitate washed with mercurous nitrate solution, dried, and heated until the weight is constant. The metal is precipitated as sulphide either in acid solution, or an ammoniacal solution is saturated with hydrogen sulphide and then acidified. The precipitate, collected in a Gooch crucible, is roasted to oxide. Molybdenite is roasted to form trioxide ; this is extracted with ammonia, and the filtrate evaporated and residue ignited (Analyst, 1906, 31, 312).

Nickel.

(*a*) As *oxide* NiO, after precipitation as nickelic hydroxide (Ni(OH)$_3$) by caustic potash or soda with the addition of bromine in absence of ammonium salts ; or after precipitation by

ammonium sulphide thoroughly saturated with hydrogen sulphide, the nickel sulphide being dissolved in aqua regia and the solution precipitated by caustic soda or potash.

(b) As *dimethylglyoxime*

$$CH_3 \cdot C : NO - Ni - NO : C \cdot CH_3$$
$$CH_3 \cdot C : NOH \qquad NOH : C \cdot CH_3$$
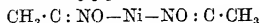
(Ni = 20·31 p.c.). A 1 p.c. alcoholic solution of dimethylglyoxime (J. pr. Chem. 1908, 77, 44) is added to a hot dilute hydrochloric acid solution of nickel followed by ammonia in slight excess. The red precipitate is collected on a Gooch crucible, washed with hot water and dried at 110°–120° (Brünck, Zeitsch. angew. Chem. 1907, 20, 834).

(c) As *nickel dicyanodiamidine* $Ni(N_4H_5C_2O)_2$. Dicyanodiamidine sulphate and caustic alkali are added to an ammoniacal solution of nickel salt, the yellow precipitate collected and dried at 115°. If cobalt is present, hydrogen peroxide is first added to the ammoniacal solution. Aluminium and iron are kept in solution by means of tartaric acid (Grossmann and Schück, Chem. Zeit. 1907, 31, 335, 911).

Platinum.

As *metal.* The solution of platinic chloride free from excess of acid is precipitated by ammonia, or, better, potassium chloride (v. Potassium), and the precipitate is filtered by Gooch's method or through a plug of thoroughly dried asbestos contained in a weighed tube. The precipitate is dried, heated to redness in a current of hydrogen, washed with water to remove alkaline chloride, again dried, and weighed. The metal is also precipitated by reducing agents (e.g. formic acid, alcohol in alkaline solution); and by metals such as magnesium or zinc (Chem. Zeit. 1905, 29, 293).

Potassium.

(a) As *platinichloride* K_2PtCl_6. The solution, which must contain the potassium in the form of chloride and be free from acid, is mixed with excess of platinic chloride and evaporated to dryness on the water-bath. The crystalline residue is washed with strong alcohol, without breaking the crystals, until the washings (which at first must be orange, showing the presence of excess of platinum) are colourless. The precipitate is left in the evaporating dish, and the washings are poured through a small filter. When washing is complete, the precipitate is transferred to a weighed porcelain crucible by means of a jet of alcohol from a wash-bottle, and the alcohol is decanted off through the filter. The precipitate in the crucible is dried first at 70° till most of the alcohol is expelled, and then at 100° for half an hour. The filter is dried, and any precipitate is detached from the paper as far as possible and added to the contents of the crucible, which is then weighed. The filter is burnt, and the ash allowed to fall into the crucible, which is again weighed. The increase in weight is filter ash and metallic platinum. The amount of platinichloride corresponding with the latter is calculated and added to the weight of the precipitate (v. J. Amer. Chem. Soc. 1895, 17, 453; and Zeitsch. anal. Chem. 1906, 45, 315; Chem. Zeit. 1906, 30, 684).

(b) As *perchlorate* $KClO_4$. The solution containing potassium and sodium as chlorides is evaporated down with excess of dilute perchloric acid until all the hydrogen chloride is expelled. The residue is taken up with alcohol, the precipitate collected on a Gooch crucible, washed with alcohol, and dried at 130° (Amer. J. Sci. 1897, 2, 263).

Selenium.

As *selenium.* The solution is strongly acidified with hydrochloric acid, mixed with excess of sulphurous acid or sodium hydrogen sulphite, and boiled for about fifteen minutes. The precipitate is collected on a weighed filter and dried at a temperature below 100°. Solutions of selenium containing hydrochloric acid cannot safely be concentrated by evaporation except in presence of a large quantity of alkaline chlorides, which prevent the volatilisation of the selenium as chloride.

Hypophosphorous acid in alkaline solution, and potassium iodide in acid solution, have also been recommended as reducing agents (Zeitsch. anorg. Chem. 41, 448; and Amer. J. Sci. 1896, [4] 1, 416). For a review of methods for estimating selenium, see Zeitsch. anorg. Chem. 1904, 41, 291).

Silver.

As *chloride* AgCl, or *bromide* AgBr. The solution is acidified with nitric acid, heated to boiling, and mixed with a slight excess of sodium chloride or potassium bromide. Estimation as bromide is to be recommended, since silver chloride is not quite insoluble in pure water. The precipitate is washed with hot water, dried, detached from the paper as far as possible, transferred to a porcelain crucible, and dried at 150°, or heated slowly until it shows signs of fusion at the edges, and weighed. The filter is burnt and the ash added to the crucible, which is again weighed. The increase in weight is filter ash and metallic silver. The quantity of bromide or chloride corresponding with the latter is calculated and added to the weight of the precipitate.

Sodium is weighed in the form of chloride together with any potassium which may be present, and is estimated by difference, or it may be estimated directly as sulphate or chloride if potassium is absent.

The following reagent precipitates sodium even from very dilute solutions, and is not interfered with by the other alkali metals or by magnesium and the metals of the alkaline earths. Three grams of bismuth nitrate and 30 grams of potassium nitrite are dissolved in water containing sufficient nitric acid to remove any turbidity, about 1·6 grams of cæsium nitrate are added, and the solution diluted with water to 100 c.c. The precipitation should be carried out in a stoppered bottle in an inert atmosphere. The precipitate, $5Bi(NO_2)_3,9CsNO_2,6NaNO_2$, contains 3·675 p.c. sodium (v. Ball, Chem. Soc. Trans. 1910, 97, 1408).

Strontium.

(a) As *sulphate* $SrSO_4$. The solution, which must contain but little free acid, is mixed with excess of dilute sulphuric acid and at least an equal volume of alcohol, and the precipitate is washed with alcohol. If alcohol cannot be used, a much larger excess of sulphuric acid is added and the precipitate is washed with cold water, but the results are less exact.

(b) As *carbonate* $SrCO_3$ (which must not be

heated too strongly) after precipitation by ammonium carbonate.

Tellurium.

(a) As *tellurium*, by reducing solutions of tellurous or telluric compounds with sulphur dioxide and hydrazine hydrochloride (Lenher, J. Amer. Chem. Soc. 1908, 30, 387). Other reducing agents have been employed: sulphur dioxide and potassium iodide, hypophosphorous acid, and grape sugar in alkaline solution.

(b) As *dioxide* TeO_2 (v. Amer. J. Sci. 1909, (iv.) 28, 112).

Thallium.

(a) As *thallous iodide* TlI. The solution is heated with sulphurous acid to reduce all the thallium compounds to thallous salts, allowed to cool, and then mixed with excess of potassium iodide. The precipitate is washed with dilute alcohol, and dried on a weighed filter at 170° (v. Baubigny, Compt. rend. 1892, 113, 544).

(b) As *thallous platinichloride*. This salt is very insoluble, but is difficult to filter (Crookes, Select Methods, 4th ed. p. 172).

Tin.

As *oxide* SnO_2, which is obtained when tin or one of its alloys is treated with nitric acid. The solution is boiled for ten minutes to ensure complete precipitation, and the precipitate is digested for an hour with dilute nitric acid (1 : 6) at 100° to remove other metals, washed with hot water, and ignited.

In other cases the tin is precipitated as hydrated oxide. If the solution contains stannous salts, the latter are oxidised by chlorine or by hydrochloric acid and potassium chlorate, ammonia added until a slight precipitate forms, and hydrochloric acid until the precipitate just redissolves. The solution is then mixed with a moderately large quantity of a strong solution of ammonium nitrate or sodium sulphate, and boiled for some time. The precipitate is washed with hot water by decantation and on the filter, dried, and heated. To ascertain if precipitation is complete, a small quantity of the filtrate is added to a hot solution of ammonium nitrate or sodium sulphate.

If the tin has been precipitated as stannic sulphide, the latter is washed with a solution of sodium chloride, and finally with a solution of ammonium acetate, dried, and roasted in a porcelain crucible until the weight is constant. Decomposition is facilitated by adding a small quantity of ammonium carbonate.

In all cases the filter is burnt separately and the ash dropped into the crucible.

Titanium.

As *dioxide* TiO_2, after precipitation by ammonia. Usually the substance is dissolved in sulphuric acid, or is fused with potassium hydrogen sulphate and dissolved in water. The solution is diluted largely and boiled for some time, when all titanium is precipitated as hydrated oxide, which is rendered anhydrous by ignition. The solution should contain 0·5 p.c. of free sulphuric acid; if less, the precipitate is impure, if more, precipitation is incomplete (Lévy). In presence of iron the results are always somewhat too high.

Baskerville recommends fusing titaniferous iron ores with potassium hydrogen sulphate containing some sodium fluoride. The product is boiled with water containing nitric acid and

then neutralised with ammonia. The precipitate is dissolved in dilute hydrochloric acid, avoiding any excess. The liquid is then saturated with sulphur dioxide and boiled, the precipitate being collected, ignited, and weighed as TiO_2 (J. Soc. Chem. Ind. 1900, 19, 419 ; also J. Amer. Chem. Soc. 1903, 25, 1073 ; and 1910, 32, 957).

Tungsten.

As *tungstic anhydride* WO_3. The solution containing the tungsten as an alkaline tungstate is neutralised with nitric acid and precipitated with a neutral solution of mercurous nitrate. The precipitate is washed with a solution of mercurous nitrate, dried, and heated in a porcelain crucible, when tungstic anhydride is left.

Fused lead tungstate, when boiled with strong hydrochloric acid, gives a precipitate of tungstic acid (Brearley, Chem. News, 1899, 79, 64).

Uranium.

(a) As the *oxide* U_3O_8. The solution, oxidised if necessary by nitric acid, is heated to boiling and mixed with a *slight* excess of ammonia. The precipitate of acid ammonium uranate is washed with ammonium chloride solution, dried, and strongly heated.

(b) As the *pyrophosphate* $(UO_2)_2P_2O_7$, obtained by precipitating uranyl ammonium phosphate $(UO_2)(NH_4)PO_4$ with ammonium phosphate in the presence of ammonium acetate and igniting the precipitate at low redness. For the application of this process to uranium minerals, see Low's Technical Methods of Ore Analysis, 3rd ed. p. 223; and J. Amer. Chem. Soc. 1901, 23, 685.

Vanadium.

(a) As *barium pyrovanadate* $2BaO \cdot V_2O_5$. The solution is neutralised with ammonia, heated to boiling, mixed with excess of barium chloride, agitated, and cooled quickly out of contact with air. The precipitate is washed and heated.

(b) As *manganese pyrovanadate* $2MnO \cdot V_2O_5$. The solution is mixed with a slight excess of ammonium chloride and ammonia, manganese chloride or sulphate mixed with ammonium chloride is added in excess, and the liquid is boiled two or three minutes and allowed to cool out of contact with the air. The precipitate, which should be brownish yellow and free from oxidation products, is washed with cold water and heated.

(c) As *pentoxide* V_2O_5, obtained (i.) by precipitating barium or lead vanadate, decomposing with sulphuric acid, filtering, evaporating the filtrate, and igniting; (ii.) by precipitating and igniting mercury vanadate; (iii.) by precipitating ammonium vanadate by ammonium chloride and igniting the precipitate.

For other methods of estimating and separating vanadium, v. A. Carnot, Compt. rend. 104, 1803 and 1850; Chem. Soc. Abstr. 1887, 896; Chem. Zeit. 1905, 29, 392 ; Amer. J. Sci. 1910, 30, 220.

Zinc.

(a) As *oxide* ZnO, with previous precipitation by sodium carbonate in absence of ammonium salts.

(b) As *sulphide* ZnS, by Rose's method after precipitating with ammonium sulphide.

The filtration of the zinc sulphide may be promoted by precipitating in the presence of ammonium acetate or thiocyanate, and washing with a 5 p.c. solution of either of these salts. If mercuric chloride is added to the solution, the mixed precipitate of mercuric and zinc

sulphides filters much better than the latter alone ; the former is expelled on ignition.

ACID RADICLES.

Carbonic acid.

The estimation of carbon in carbonates may be made by a loss in weight method. The carbonate is weighed into an apparatus fitted with a stoppered dropping funnel containing acid to decompose the carbonate, and an exit tube containing strong sulphuric acid to dry the escaping gas. The apparatus is weighed with the acids, &c., after the carbonate has been introduced. The acid is then allowed to drop on the carbonate until the decomposition is complete, and the liquid boiled to expel dissolved carbon dioxide. The apparatus is again weighed and the loss of weight gives the amount of carbon dioxide. The apparatus is figured in most treatises on quantitative analysis. More accurate results are obtained by weighing the carbon dioxide directly by absorbing it in weighed tubes containing soda lime or in bulbs containing aqueous caustic potash. For a complete form of apparatus for this estimation, see Thorpe's Quantitative Analysis, 9th ed. p. 86, and Clowes and Coleman's Analysis, 8th ed. p. 104.

When carbonates and sulphides occur together, the gases evolved on treatment with acid are passed into a solution of copper acetate acidified with acetic acid and heated to boiling. Hydrogen sulphide is absorbed, with formation of copper sulphide, and carbon dioxide passes on.

For the estimation of carbon dioxide in the presence of nitrites, sulphides, and sulphites, see Marle, Chem. Soc. Trans. 1909, 1491 ; and Wolkowitz, Zeitsch. angew. Chem. 1894, 165.

Chloric acid.

Any chlorine present as chloride is determined, the chlorate reduced by a zinc-copper couple, and the chlorine again determined. The difference is the amount of chlorine existing as chlorate (Thorpe, Chem. Soc. Trans. 1873, 541). Thin granulated zinc is washed with caustic soda solution, then with dilute sulphuric acid, which is allowed to act for a short time, and finally with water. It is then covered with about 100 c.c. of a 3 p.c. solution of copper sulphate heated to $40°-50°$. When most of the copper has been deposited, the liquid is carefully poured off, and treatment repeated with a fresh quantity of solution. The zinc-copper couple is now very carefully washed with distilled water by decantation, not more than 0·5 gram of potassium chlorate, or the equivalent quantity of any other chlorate, is weighed out into the beaker and dissolved in about 25 c.c. of warm water, which should just cover the couple. The liquid is heated gently for half an hour, then boiled for half an hour, dilute sulphuric acid added drop by drop until the white precipitate of zinc hydroxide and oxychloride just dissolves, filtered, the filtrate neutralised with pure calcium carbonate, and the chlorine estimated by standard silver nitrate solution (Chem. Soc. Trans. 1888, 166).

This reduction may also be effected by Devarda's alloy (Al 45, Zn 5, Cu 50). Jannasch recommends hydroxylamine sulphate and excess of nitric acid as a suitable reducing agent for chlorates while bromates and iodates are best reduced by hydroxylamine in ammoniacal solution (Ber. 1905, 38, 1576). Formaldehyde in dilute nitric acid reduces chlorates in 30 minutes and bromates in $2\frac{1}{2}$ hours: iodates are not reduced (Grützner. Arch. Pharm. 1896, 294, 634 ; compare Brunner and Mellet, J. pr. Chem. 1908, 77, 33).

Hydrobromic, hydrochloric, and hydriodic acids.

As silver salts (AgBr, AgCl, AgI). The solution is mixed with excess of silver nitrate, acidified with nitric acid, and heated to boiling. The precipitate is treated exactly as in the estimation of silver.

Hydrofluoric acid.

(a) As *calcium fluoride* CaF_2, in the case of soluble fluorides. The solution is mixed with a moderate excess of sodium carbonate, heated to boiling, and mixed with excess of calcium chloride. The precipitate is washed, dried, and heated to redness in a platinum crucible, then treated with excess of acetic acid, evaporated to dryness, and heated to expel excess of acid. The product is now heated with water, and the insoluble calcium fluoride filtered off, washed, and heated.

(b) Indirectly as *silicon fluoride* SiF_4. The finely powdered solid substance is placed in a deep platinum crucible and covered with three or four times its weight of pure precipitated silica, the weight of which is accurately known. Sulphuric acid is then added, and the crucible gently heated for half an hour. The temperature is raised to expel most of the sulphuric acid, the residue treated with hydrochloric acid, washed, dried, and heated. The hydrofluoric acid is calculated from the loss in weight of the silica : $4HF = SiO_2$. The amount of silica in the substance must be known, and its weight added to that of the admixed silica.

(c) By *distillation and weighing as calcium fluoride.* The fluoride is decomposed by concentrated sulphuric acid in a platinum apparatus ; the hydrogen fluoride carried off in a current of air and carbon dioxide and absorbed in a solution of pure caustic soda contained in a platinum dish. Calcium chloride is added to this solution and the precipitate ($CaCO_3$ and CaF_2) washed, ignited, and treated with dilute acetic acid in moderate excess. After evaporation to expel this excess of acid, the residue is taken up with water and the insoluble calcium fluoride collected, washed, and ignited (Jannasch and Röttgen, Zeitsch. anorg. Chem. 1895, 9, 267). The apparatus employed is figured in Jannasch's Praktischer Leitfaden der Gewichtsanalyse, 2nd ed. 411 (compare also J. Amer. Chem. Soc. 1901, 23, 825 ; and Chem. News, 1905, 92, 184).

(d) Directly as *silicon fluoride* (Fresenius). The mineral is finely powdered and intimately mixed with ignited quartz and heated with concentrated sulphuric acid in a dry U-tube at $150°-160°$. A current of dry air free from carbon dioxide is drawn through the decomposition tube and thence through a series of five U-tubes. The first of these is empty and cooled by immersion in cold water ; the second contains glasswool, or, if the substance contains chlorine, half is filled with pumice impregnated with anhydrous copper sulphate, and the other half with pure dry calcium chloride. The third and fourth tubes

are weighed and serve to absorb the silicon fluoride ; the third contains pumice moistened with water, and the fourth contains soda lime and calcium chloride. The fifth tube is a guard tube containing the same reagents as the fourth. After one or two hours the decomposition of the fluoride is complete, and the gain in weight of the absorption tubes represents the amount of silicon fluoride generated. This process may be rendered volumetric (*v. Volumetric section*).

Hydrogen sulphide (sulphides).

Insoluble sulphides are decomposed by hydrochloric acid in a flask similar to that used in the gravimetric estimation of carbonic acid, and the gas evolved is led into two or three bulb U-tubes containing a solution of bromine in dilute hydrochloric acid, which converts the hydrogen sulphide into sulphuric acid. When decomposition is complete, the liquid in the flask is boiled, and the last traces of the gas are drawn through the bulbs by means of an aspirator. The contents of the bulb tubes are transferred to a beaker, heated to expel bromine, and the sulphuric acid precipitated by barium chloride.

Sulphides which are not decomposed by hydrochloric acid may be oxidised with aqua regia, hydrochloric acid and bromine, or hydrochloric acid and potassium chlorate, the sulphuric acid formed being weighed as barium sulphate.

Nitric acid.

(*a*) Indirectly, as ammonia, by means of the zinc-copper couple (Thorpe). A zinc-copper couple (*v. Chloric acid*) is made in a flask into which is weighed a quantity of the nitrate corresponding with not more than 0·5 gram of potassium nitrate, and sufficient water is added to just cover the couple. The flask is attached to a condenser, the other end of which is connected with a U-tube or flask containing hydrochloric acid, as in the estimation of ammonia. The liquid is gently heated for some time, and then distilled nearly to dryness. After cooling, a further quantity of water is added to the couple, and distillation repeated. The ammonia in the distillate is estimated as platinichloride, or is received in a measured volume of standard acid and titrated. The reduction can also be conveniently effected by the use of Devarda's alloy (*v. Chloric acid*) in alkaline solution (Analyst, 1910, 35, 307).

(*b*) *Schloesing's method.* When a solution of a nitrate is heated with an acid solution of a ferrous salt, the nitrate is decomposed, the whole of the nitrogen being evolved as nitric oxide, which is measured. The difficulty lies mainly in obtaining the nitric oxide free from air. The apparatus employed consists of a *small* distilling flask provided with a side tube which terminates under a gas-collecting tube in a mercurial trough. The neck of the flask is fitted with a cork, which carries a tube funnel provided with a stop-cock and another tube connected with a carbon-dioxide apparatus. Carbon dioxide *free from air* is passed into the apparatus until all air is expelled and the gas issuing from the exit tube is completely absorbed by caustic potash. The substance containing the nitrate, which must be in the solid condition, is dissolved in 2 or 3 c.c. of concentrated ferrous chloride solution, mixed with 1 c.c. of strong hydrochloric acid, and introduced into the flask by means of the funnel tube, care being taken that no air

enters. The dish and the funnel are rinsed with very small quantities of acid, the object being to use as little liquid as possible. The contents of the flask are then rapidly boiled to dryness, the evolved gas being collected in the tube over mercury, and carbon dioxide is driven through the apparatus to expel all nitric oxide. The mixture of nitric oxide and carbon dioxide is transferred to an apparatus for gas analysis ; the latter absorbed by caustic potash, and the former mixed with oxygen and absorbed by alkaline pyrogallol. Nitrites are converted into nitrates by addition of hydrogen peroxide during evaporation of the original solution (*v.* Warington, Chem. Soc. Trans. 1880, 468, and 1882, 345).

(*c*) *By standard indigo solution* (Warington, Chem. News, 35, 45, and Chem. Soc. Trans. 1879, 578).

(*d*) As 1 : 4-*diphenyl*-3 : 5-*endanilodihydrotriazole nitrate* $C_{20}H_{16}N_4$,HNO_3. A 10 p.c. solution of the base 1 : 4-diphenyl-3 : 5-endanilohydrotriazole 'Nitron,'

$$C_6H_5 \cdot N \underset{N \cdot C_6H_5}{\overset{N \cdot C_6H_5}{\underset{}{\big|}}} \quad N$$
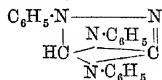
in 5 p.c. acetic acid produces a voluminous white precipitate in dilute nitric acid or nitrate solution. Nitrites interfere by giving a sparingly soluble salt with this base ; they are removed by hydrazine sulphate. Bromides, iodides, chlorates, perchlorates, and chromates, are also precipitated by nitron, and must be removed. Organic matters do not seriously affect the method, which has been tested successfully with solutions containing 0·5 p.c. of gelatine, and 2 p.c. of dextrin (Busch, Ber. 1905, 38, 861). The method gives favourable results for nitrates in water or fertilisers (Collins, Analyst, 1907, 32, 349).

(*e*) Howard and Chick have shown that cinchonamine gives a very insoluble nitrate and can be used in estimating nitric acid and its salts (J. Soc. Chem. Ind. 1909, 28, 53).

Oxalic acid.

As *calcium oxalate.* The method is already indicated under *Calcium.*

Phosphoric acid.

As *magnesium pyrophosphate* $Mg_2P_2O_7$. The operation is conducted as in the estimation of magnesium. If magnesium sulphate is used as the precipitant, the precipitate may be contaminated with basic magnesium sulphate ; it is therefore advisable to employ a solution of the chloride, which is made as follows : 85 grams of crystallised magnesium sulphate are dissolved in boiling water, acidified with 5 c.c. of hydrochloric acid, mixed with an aqueous solution of 82 grams of crystallised barium chloride, boiled, and filtered. A few drops of magnesium sulphate solution are added to be sure that there is no excess of barium, then 165 grams of pure ammonium chloride, and 260 c.c. of ammonia, and the solution diluted to 1 litre. After two or three days the solution is filtered. In many cases the phosphoric acid is first separated by ammonium molybdate (*v. Methods of separation*).

Silicic acid.

As *silica* SiO_2. Soluble silicates are acidified with hydrochloric acid and evaporated to complete dryness ; moistened with strong hydro-

chloric acid, again evaporated to dryness, the residue treated with dilute acid, and the insoluble silica washed with hot water and ignited.

Insoluble silicates are very finely powdered, intimately mixed with about five times their weight of a dry mixture of sodium and potassium carbonates in equal proportions, and heated to redness in a platinum crucible for half an hour. The cooled mass is treated with water, acidified with hydrochloric acid, and evaporated as above.

(For the separation of silica when the alkalis have to be estimated, *v. Methods of separation,* Group VI.)

Sulphuric acid.

As *barium sulphate* BaSO$_4$, by precipitation with barium chloride. The chief difficulty arises from the tendency of the barium sulphate to separate in a finely divided condition and to carry down impurities, especially in presence of nitrates and potassium salts. These sources of error are avoided by taking care that the solution is somewhat dilute, is free from nitrates, and contains a moderate but not excessive quantity of free hydrochloric acid. The solution and the barium chloride solution should both be heated to boiling, and mixed *gradually, with continual agitation.* The liquid may be filtered as soon as it has become clear, and the precipitate is washed with hot water and heated to dull redness. If too little hydrochloric acid is present, the precipitate is liable to be impure ; if a very large excess of the acid is present, precipitation is not quite complete (compare Allen and Johnston, J. Amer. Chem. Soc. 1910, 32, 588).

Sulphurous acid.

Indirectly as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

Thiosulphuric acid.

Indirectly as barium sulphate after oxidation by bromine water, excess of bromine being expelled by boiling.

Water is usually estimated by difference. If a direct determination is required, the method to be adopted will depend upon circumstances. In many cases it is sufficient to heat the substance on a watch-glass, or in a crucible in a drying oven, at a definite temperature, until the weight is constant. During weighing the dried substance must be carefully protected from the air. Attention must, however, be paid to the possibility of the volatilisation of substances other than water. Many hydrated haloid salts, for example, lose part of their acid. In such cases the substance is previously mixed with a known weight of perfectly dry lead monoxide. Ammonia, ammonium salts, and volatile organic matter may also be given off. If the drying is conducted in a glass tube, the vapours may be led into standard acid and the ammonia determined by titration : the total loss, *minus* the ammonia, gives the amount of water. Some substances increase in weight in consequence of oxidation. Frequently it is desirable to collect the evolved water and weigh it directly. The substance is introduced into a glass tube (plain, or with a bulb in the middle) drawn out and bent at right angles at one end, which passes directly, without any intervening indiarubber tube, through the cork of a **U**-tube containing either calcium chloride or pumice moistened with strong sulphuric acid (*v.* ORGANIC ANALYSIS).

All fluosilicates, even topaz, evolve silicon fluoride on ignition, and water is estimated by mixing the mineral with lead oxide in a hard glass tube, heating the mixture in a current of dry air and passing the gases over a layer of lead oxide contained in the same tube. The water is collected and weighed in calcium chloride tubes.

METHODS OF SEPARATION.

A. *The Estimation of the Metals in their Ores and Alloys.*

In this section the metals are arranged in the order in which they occur in the qualitative groups. Both gravimetric and volumetric methods are included in this description, the latter being indicated wherever possible, owing to the greater rapidity with which the analysis can be executed.

GROUP I.

Silver is separated from all other metals by treating its ores and alloys with moderately strong nitric acid, evaporating off excess of solvent, diluting with water, and adding to the filtered solution either hydrochloric acid or sodium chloride. To remove any lead or thallous chloride which may be present, the precipitate is extracted repeatedly with warm water ; it should, however, be remembered that silver chloride is not absolutely insoluble in hot water. Silver is conveniently estimated volumetrically in the above dilute nitric acid solution, after boiling off nitrous fumes, by adding ferric indicator and titrating with standard ammonium thiocyanate in accordance with Volhard's method (*see Volumetric section*). The presence of other metals having colourless salts does not interfere with this process ; nickel, cobalt, and copper must not be present to any large extent, and mercury should be absent because of the insolubility of mercuric thiocyanate. When more than 60 p.c. of copper is present, the silver is precipitated with excess of alkali thiocyanate. The well-washed silver thiocyanate is decomposed by strong nitric acid, the sulphuric acid produced precipitated by barium nitrate, and the Volhard titration effected without filtering off the barium sulphate (*v.* Ber. 1905, 38, 566).

The silver in argentiferous galena is estimated by fusing the sulphide with crude potassium hydrogen tartrate (argol), and sodium carbonate in an iron crucible, and by heating the lead-silver button thus obtained in a porous bone-ash crucible (' cupel ') until the lead is removed as oxide, partly by volatilisation and partly by absorption into the cupel. The residual silver is detached from the cold cupel and weighed.

Gold quartz is assayed for silver by heating the mineral with lead oxide, and a reducing flux, when the lead produced extracts both the gold and silver. This alloy is cupelled, and the silver-gold button is ' parted ' by heating with strong nitric acid diluted with three parts of water ; the residual gold is collected, ignited, and weighed. The silver is precipitated by hydrochloric acid from the nitric acid solution. When more than 30 p.c. of gold is present in the button for parting, this metal will retain silver. In order to prevent this retention, a known weight of silver is added to the fused button. (For further details of the separations of gold, silver, and lead in the dry way, see ASSAYING, pp. 322-327.)

Thallium, in the more stable thallous condition to which thallic salts are readily reduced, is separated from the metals of Group II. by precipitating the latter with hydrogen sulphide in acid solution. Alkali hydroxides separate it from all metals, giving insoluble hydroxides, and ammonium sulphide, which precipitates thallous sulphide, separates this metal from the alkalis and alkaline earths. Gravimetrically, thallium can be weighed as acid sulphate TlHSO₄, stable at 240°, and as sulphate Tl_2SO_4, stable at low red heat; it can be precipitated and weighed as iodide TlI, platinichloride Tl_2PtCl_6, and chromate Tl_2CrO_4. Volumetrically, it can be estimated by the oxidation of thallous salts by permanganate or by titrating with thiosulphate the iodine set free in accordance with the following reaction: $TlCl_3 + 3Kl = TlI + 3KCl - I_2$ (Chem. Soc. Proc. 1908, 24, 75).

GROUP II.

Mercury in its ores is generally estimated by distillation with quicklime in a current of coal gas or carbon dioxide. The decomposition of the mercury compounds is facilitated by mixing copper strips with the quicklime, and the presence of this reducing agent is essential in the case of mercuric iodide. The mercury which distils over is collected under water, washed, dried, and weighed. Ores containing only small amounts of mercury are decomposed by heating
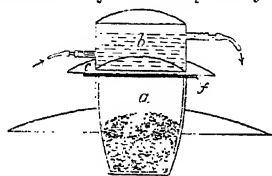
FIG. 8.

with iron filings in a porcelain crucible, *a*, having a silver lid, *f*, which is cooled by a water-jacket, *b*, laid upon it. The mercury condenses on the under surface of the silver plate, *f*, which is weighed before and after the experiment (*v.* Holloway, Analyst, 1906, 31, 66).

Mercury is separated from all other metals in the wet way by dissolving the ore or alloy in nitric acid or aqua regia, diluting considerably, precipitating the sulphides of Group II. by hydrogen sulphide, removing the arsenic-tin sub-group by means of yellow ammonium sulphide (*not* sodium sulphide or hydroxide), treating the residual sulphides with dilute nitric acid (sp.gr. 1·2–1·3), and dissolving the final residue in aqua regia and filtering if necessary from sulphur and lead sulphate. The mercury can be reprecipitated by almost neutralising the acid solution, adding in succession ammonium sulphide, caustic soda and ammonium nitrate. The caustic soda redissolves the sulphide initially formed as the soluble double sulphide Hg(SNa)₂, and from this the ammonium nitrate reprecipitates mercuric sulphide in a form suitable for collection. The precipitate is washed successively with water, alcohol, and carbon disulphide, dried at 110°, and weighed as HgS. (For other methods of separating mercury, see Jannasch, Zeitsch. anorg. Chem. 1896, 12, 132, and 359; and Stähler, Chem. Zeit. 1907, 31, 615.)

Lead in its ores and alloys is usually separated from other metals by dissolving the substance in hydrochloric or nitric acid, or if necessary in a mixture of the two acids, and evaporating down the solution with sulphuric acid until white fumes are evolved. The mixture is then cooled diluted with water, and the lead sulphate quickly collected. If the amount of lead is small, alcohol must be added to complete the precipitation. The lead sulphate thus obtained is freed from silica, stannic oxide, and other impurities by dissolving it in an excess of ammonium or sodium acetate.

When separated as lead sulphate, the lead can be estimated volumetrically by boiling the precipitate with ammonium carbonate and then dissolving the lead carbonate in acetic acid. The lead is thus converted into lead acetate which is titrated with standard ferrocyanide using as indicator drops of uranium acetate on a porcelain plate. The lead may also be reprecipitated as oxalate from the acetate solution by alkali oxalate, the washed lead oxalate being then suspended in dilute sulphuric acid, and titrated with standard permanganate. From the solution of the sulphate in sodium acetate the lead can be precipitated as chromate by potassium dichromate. The chromate is dissolved in dilute nitric acid, and reduced with methyl or ethyl alcohol. The solution, rendered ammoniacal, is treated with oxalic acid, when lead is precipitated and titrated as above with standard permanganate (*v.* Chem. News, 1896, 73, 18; J. Amer. Chem. Soc. 1896, 18, 737; Zeitsch. anal. Chem. 1902, 41, 653). Lead may be separated from copper by electrolysing a solution of the metals in dilute nitric acid with a weak current (0·5–1·5 amperes and 1·4 volts), when the lead is precipitated as dioxide on the anode (a platinum dish with unpolished inner surface).

Bismuth is separated from all other metals but those of Group II. by the precipitation of its sulphide by hydrogen sulphide in acid solution. The insolubility of the sulphide in ammonium sulphide separates this metal from arsenic, antimony, and tin. The further separation of bismuth from mercury, copper, and cadmium presents no particular difficulty, and is effected by taking advantage of the solubility of bismuth sulphide in nitric acid (sp.gr. 1·25), and the precipitation of bismuth oxychloride on diluting considerably an acid solution of bismuth chloride. The problem of separating bismuth from lead is, however, much more troublesome, and the following appear to be most trustworthy methods: (i.) the separation of the bismuth as basic nitrate and the solution of lead nitrate in dilute ammonium nitrate (J. pr. Chem. 1858, 74, 345); (ii.) the distillation of the mixed sulphides in a current of bromine, when bismuth bromide is volatilised, leaving behind lead bromide (Jannasch, Praktischer Leitfaden der Gewichtsanalyse, 1st ed. 155); (iii.) the precipitation of bismuth as the basic formate; a repetition of this operation gives a precipitate free from lead, which is dissolved in dilute nitric acid, the solution almost neutralised with sodium carbonate, and the bismuth then finally precipitated and weighed as phosphate $BiPO_4$ (Stähler, Chem. Zeit. 1907, 31, 615). The lead in the filtrate from the formate separation is precipitated as sulphide, converted into sulphate, and weighed as such. This method

of separation gives accurate results (Little and Cahen, Analyst, 1910, 35, 301).

Copper is separated from the metals of Groups III., IV., V., and VI., by precipitation as sulphide by hydrogen sulphide in acid solution. In alloys and ores it is generally separated from antimony and tin by rendering these insoluble by the action of moderately strong nitric acid. If, however, the sulphides of these metals and arsenic are present, they are extracted from the precipitate with alkali sulphides (not ammonium sulphide). The insoluble residue, containing the sulphides of copper, bismuth, lead, mercury, and cadmium, is treated with nitric acid (*v. Mercury* and *Bismuth*). Copper is readily separated from bismuth by means of ammonium carbonate, which precipitates basic bismuth carbonate, leaving copper in solution. The separation from cadmium may be effected by one of the following methods :—(1) Hydrogen sulphide is passed into a boiling solution of the sulphates of copper and cadmium in dilute sulphuric acid (1 : 4). The precipitated copper sulphide, which contains some cadmium, is redissolved in nitric acid, and, after expelling excess of the solvent, the precipitation is repeated. (2) The copper is precipitated as cuprous thiocyanate, leaving cadmium in solution. (3) The copper is converted into potassium cuprocyanide $K_3Cu(CN)_4$, with a considerable excess of potassium cyanide, and the cadmium precipitated with hydrogen sulphide or ammonium sulphide (compare also Browning, Amer. J. Sci. 1893, [3] 46, 280).

The following volumetric processes for copper are employed in the technical analysis of the ores of this metal. (i.) The mineral is dissolved in hydrochloric and nitric acids, and the solution boiled down with sulphuric acid to expel the volatile acids. The copper is precipitated from the boiling solution by introducing a sheet of aluminium and redissolving in nitric acid with the addition of bromine to destroy nitrous fumes. The solution is neutralised with ammonia, acidified with acetic acid, and treated with excess of potassium iodide, when the liberated iodine is titrated with standard thiosulphate (Low, J. Amer. Chem. Soc. 1902, 24, 1082). (ii.) A solution of potassium cyanide is standardised against pure copper foil by dissolving the latter in nitric acid, adding bromine, boiling to expel nitrous fumes and excess of bromine, adding ammonia till strongly alkaline, and titrating with the cyanide solution until the blue tint disappears. The copper ore is treated as in (i.), the copper being precipitated by aluminium, redissolved in nitric acid, and the resulting solution titrated in manner just described (*v.* Brearley, Chem. News, 1897 76, 189). (For other methods of separating and estimating copper, see also Zeitsch. anorg. Chem. 1896, ii. 268 ; Chem. Soc. Abstr. 1901, ii. 197 ; J. Amer. Chem. Soc. 1905, 27, 1224; Zeitsch. anal. Chem. 1907, 46, 128 ; J. Amer. Chem. Soc. 1908, 30, 760; Chem. Zeit. 1908, 33, 263; Amer. J. Sci. 1909, (iv.) 27, 448.) (For electrolytic estimation of copper, *see* p. 250.)

Cadmium is separated from the other metals of Group II. by the methods indicated under *copper, lead, &c.* In the presence of zinc, Fox recommends precipitation in a solution containing trichloroacetic acid (Chem. Soc. Trans. 1907, 91, 964). Electrolytically, cadmium is

deposited from a cyanide solution (0·7–1·2 amperes and 4·8–5 volts); the use of a rotating cathode accelerates the rate of deposition (compare Flora, Amer. J. Sci. 1906, 70, 268 and 392; and Avery and Dales, J. Amer. Chem. Soc. 1897, 19, 379).

Tin, antimony, and *arsenic* are separated from the remaining metals of Group II. by digesting the group precipitate at 80° with concentrated yellow ammonium sulphide, when the sulphides of these three metals dissolve, leaving the other sulphides insoluble. Copper sulphide is appreciably soluble in this solvent, and in the presence of copper it is preferable to use sodium or potassium sulphide, but in the presence of mercury these reagents are inadmissible, owing to formation of the soluble double sulphide $Hg(SK)_2$. In the presence of much lead a small amount of tin is retained in the insoluble residue. Arsenic rarely occurs in alloys, and in these substances antimony and tin are separated from other metals as insoluble oxy-acids (metantimonic and metastannic acids) by the use of nitric acid as solvent.

Arsenic is separated from antimony and tin by distilling the hydrochloric acid solution of the three elements with ferrous chloride; the arsenic is volatilised as arsenious chloride; this compound is collected in cold water and the arsenic precipitated as trisulphide (Fischer, Zeitsch. anal. Chem. 1881, 21, 266). Various modifications of this method have been introduced; the distillation is carried on in a current of hydrogen chloride and hydrogen sulphide, the latter serving as the reducing agent instead of ferrous chloride ; the volatilised arsenious chloride is converted in the cooled receiver into the trisulphide (Piloty and Stock, Ber. 1897, 30, 1649). (For other modifications, *see* Gooch and Danner, Amer. J. Sci. 1891, [3] 42, 308; Andrews, J. Amer. Chem. Soc. 1895, 17, 869; Rohmer, Ber. 1901, 34, 33 ; Morgan, Chem. Soc. Trans. 1904, 85, 1001.)

The arsenic may also be separated from tin and antimony by dissolving the three sulphides in ammoniacal hydrogen peroxide, neutralising the solution with mineral acid, acidifying with tartaric acid, and precipitating the arsenic as magnesium ammonium arsenate by the addition of ammonia and magnesia mixture (*see Qualitative analysis*).

The following method of separating arsenic and antimony in their ores, leads to volumetric processes for the determination of these elements (Low, J. Amer. Chem. Soc. 1906, 28, 1715). The mineral is decomposed by heating with strong sulphuric acid (20 parts) containing potassium hydrogen sulphate (1·4 parts), and 1 part of tartaric acid. The cooled product is taken up with 350 c.c. of hot water, 10 c.c. of strong hydrochloric acid, and 3 grams of tartaric acid, and the solution saturated with hydrogen sulphide. The mixed sulphides are dissolved in aqueous potassium sulphide, and the filtrate evaporated down with 10 c.c. of strong sulphuric acid and 3 grams of potassium hydrogen sulphate until the sulphur and the greater part of the free aid are expelled. The cooled melt is dissolved in 50 c.c. of strong hydrochloric acid and 25 c.c. of water, and arsenious sulphide precipitated by hydrogen sulphide. The antimony remaining in the filtrate is precipitated as sulphide by

diluting the solution and passing in more hydrogen sulphide. The antimonious sulphide is again dissolved in potassium sulphide, the solution evaporated nearly to dryness with strong sulphuric acid and potassium hydrogen sulphate, the melt dissolved in dilute hydrochloric acid and titrated with standard permanganate.

The arsenious sulphide is dissolved in warm ammonium sulphide, and the solution heated strongly with strong sulphuric acid and potassium hydrogen sulphate until all the sulphur and nearly all the acid are expelled. The residue is boiled with water to expel sulphur dioxide, neutralised, and titrated with standard iodine solution in the presence of sodium bicarbonate.

Arsenic may also be estimated in minerals (which do not contain phosphates) by fusing the powdered ore with sodium carbonate and nitre or sodium peroxide, extracting the fused mass with water and precipitating silver arsenate from the neutralised solution. This precipitate is redissolved in nitric acid, and the amount of silver in it determined by standard thiocyanate; whence the quantity of arsenic present can be readily calculated. (For other processes for the estimation of arsenic is technically important materials, v. Clark, Chem. Soc. Trans. 1892, 61, 424; Friedheim, Zeitsch. anal. Chem. 1905, 44, 665; Heath, Zeitsch. anorg. Chem. 1908, 59, 87; Gooch and Phelps, Amer. J. Sci. 1906, (iv.) 22, 488; McGowan and Floris, J. Soc. Chem. Ind. 1905, 24, 265; Sanger and Black, ibid. 26, 1115.) (For the detection and estimation of minute quantities of arsenic, v. ARSENIC.)

Separation of tin and antimony. In the absence of any large amount of lead or other metal giving a sulphide insoluble in ammonium sulphide, tin and antimony can be separated from these metals by means of this reagent, but if lead is present in considerable amount the tin is never completely extracted, a portion always remaining in the insoluble residue. In this case it is preferable to separate out the tin and antimony by oxidising them to their insoluble hydrated oxides by means of nitric acid. These oxides when fused with caustic soda in a silver crucible yield sodium stannate and antimonate; the latter of these salts is practically insoluble in dilute alcohol (1 vol. alcohol, 2 vols. water), whilst the former is readily dissolved. A repetition of this process with the insoluble antimonate leads to a complete separation.

When present as sulphides, these metals are conveniently dealt with by Henz's modification of Clark's method. The sulphides are dissolved in excess of aqueous caustic potash containing potassium tartrate; the solution is gradually heated to boiling with excess of 30 p.c. hydrogen peroxide. When the oxidation of the sulphides is complete, excess of oxalic acid is added (15 grams for 1 gram of mixed metal), the liquid boiled to destroy excess of hydrogen peroxide, and hydrogen sulphide passed for some time through the hot solution. The precipitated antimony sulphide is dealt with as described under gravimetric estimations (p. 180). The filtrate is treated with sulphuric acid, concentrated to a small bulk (150 c.c.), and electrolysed at 60° with a current of 0·2–0·3 ampere, and 2·3 volts, using a rotating anode, when the de-

position of the tin is complete in about one hour (Henz. Zeitsch. anorg. Chem. 1903, 37, 1; and Cahen and Morgan, Analyst, 1909, 34, 3).

In Clark's original process the filtrate from the antimony sulphide, which contains stannic tin, is mixed with yellow ammonium sulphide in excess and acidified with acetic acid. After some time the stannic sulphide is collected, washed with a solution of ammonium nitrate, and converted into stannic oxide by ignition. In accurate work the antimony sulphide is redissolved, and the oxalic acid separation repeated in order to obtain the last traces of tin (compare Carnot, Compt. rend. 1886, 103, 258). For descriptions of other methods of estimating tin and antimony in their ores and alloys, see J. Soc. Chem. Ind. 1892, 11, 662; G. W. Thompson, J. Soc. Chem. Ind. 1896, 15, 179; T. Brown, jun., J. Amer. Chem. Soc. 1899, 21, 780; Argenot, Zeitsch. angew. Chem. 1904, 17, 1274; Lévy, Analyst, 1905, 30, 361; Panajotow, Ber. 1909, 42, 1296.)

The following process, due to Pearce, gives a rapid volumetric method for estimating tin in its ores. The mineral is fused in a nickel crucible with about 20 parts of sodium hydroxide with the addition of a little powdered charcoal; the fused mass is dissolved (excepting silica) in hydrochloric acid, and the solution reduced by the addition of iron rods or sheet nickel. The stannous chloride thus produced is titrated with standard iodine solution in presence of sufficient hydrochloric acid (1 : 4) to prevent the oxidation of any arsenic or antimony which may be present.

Gold and *platinum* are separated chiefly in the analytical subgroup containing arsenic, antimony, and tin. Fusion of the sulphides with sodium carbonate and nitre, followed by extraction with water, removes the arsenic. The residue, treated with zinc and hydrochloric acid, reduces tin and antimony to the metallic state; the former is dissolved by boiling hydrochloric acid, and the latter by nitric and tartaric acids, whilst gold and platinum are left. Treatment of the mixed metals with chlorine water removes gold, and dilute *aqua regia* then dissolves platinum, palladium, and rhodium. From this solution platinum is precipitated by ammonium chloride and alcohol, and from the filtrate, after neutralisation with sodium carbonate, palladium is precipitated as cyanide by mercuric cyanide.

The residue from the *aqua regia* treatment is roasted in the air; osmium volatilises as the tetroxide, ruthenium sublimes as the dioxide, whilst iridium is left (v. Leidié, Compt. rend. 1900, 131, 888; and PLATINUM METALS).

Molybdenum is precipitated as sulphide preferably from a sulphuric acid solution by treatment with hydrogen sulphide under pressure. From the sulphides of the copper-lead subgroup, it is separated by digestion with sodium sulphide under pressure, when the molybdenum passes into solution and is reprecipitated as sulphide by dilute sulphuric acid. Molybdenum sulphide is separated from the sulphides of antimony and tin by dissolving the latter in hydrochloric acid. The sulphides of arsenic and molybdenum are dissolved in hydrochloric acid and potassium chlorate, the arsenic precipitated from the filtrate after adding ammonia and magnesia mixture as magnesium ammonium

arsenate. The final filtrate is acidified, and the molybdenum reprecipitated as sulphide. Molybdenum is separated from phosphorus in a similar manner. From tungsten it is best separated by heating the mixed trioxides or their alkali salts at 250°–270° in a current of hydrogen chloride, when the molybdenum is completely volatilised as the additive compound $MoO_3,2HCl$, while the tungsten remains in the non-volatile residue (Debray, Compt. rend. 1858, 46, 1101 : and Péchard, *ibid.* 1892, 114, 173).

Selenium and *tellurium* fall into the analytical sub-group containing arsenic, and after this element has been removed as magnesium ammonium arsenate (*v. Molybdenum*), the selenium and tellurium are precipitated by reducing agents such as sulphur dioxide, hydrazine, &c. (i.) Sulphur, selenium, and tellurium are separated by fusion with potassium cyanide in a stream of hydrogen. On dissolving the mass in water and passing air through the solution, the potassium telluride present is decomposed, and tellurium is precipitated. When the filtrate is acidified, the potassium selenocyanate (KCNSe) is decomposed, yielding selenium. (ii.) The mixed dioxides of selenium and tellurium are dissolved in aqueous caustic potash ; the solution, faintly acidified with hydrochloric acid, is diluted to at least 200 c.c. with boiling water, rendered just ammoniacal and reacidified with acetic acid. After 30 minutes the tellurium dioxide is collected, washed with cold water, and gently ignited (Browning and Flint, Zeitsch. anorg. Chem. 1909, 64, 104).

Gold from all other metals : reduction of an acid solution by oxalic acid or sulphurous acid.

Selenium from the metals : reduction with sulphurous acid in hydrochloric acid solution.

GROUP III.—The metals of Group IIIa. are separated from those of the succeeding groups by precipitation with ammonia in presence of ammonium chloride ; the metals of Group IIIb. are separated from those of the succeeding groups by means of ammonium sulphide (*v. General methods of estimation*).

Iron, aluminium, chromium, uranium, glucinum, and cerium, from zinc, manganese, nickel, cobalt. The solution, which must contain iron and uranium as ferric and uranic salts, is nearly neutralised, mixed with excess of finely divided and recently precipitated barium carbonate, and allowed to remain in a closed vessel at the ordinary temperature for some hours with occasional agitation. In presence of nickel and cobalt, ammonium chloride should be added to prevent precipitation of traces of these metals. Filter and wash with cold water. The precipitate may contain ferric, chromic, aluminium, glucinum, ceric and uranic hydroxides, mixed with barium carbonate ; the filtrate contains the other metals, together with some barium. In both cases the barium can be removed by means of sulphuric acid, but as the barium sulphate carries down small amounts of the other metals, it is preferable to separate the metals of Groups III. and IV. by a double precipitation with ammonium sulphide (Treadwell).

Iron and aluminium from zinc, manganese, nickel, cobalt, uranium, and metals of the succeeding groups. The solution, which must contain iron as a ferric salt, is nearly neutralised by

sodium or ammonium carbonate. In presence of iron the liquid becomes deep red, but no precipitate must be formed. Sodium, or, better, ammonium acetate, is added in sufficient but not excessive quantity, and the liquid is boiled until the precipitate becomes granular and settles rapidly. Prolonged boiling makes the precipitate slimy. The liquid is filtered whilst hot, and the precipitate is washed with hot water ; if the liquid is allowed to cool the precipitate is partially redissolved. The precipitate is converted into ferric and aluminium oxides by ignition ; the other metals are in the filtrate. It is advisable, and in presence of nickel essential, to redissolve the precipitate and repeat the process. This method is not available for the separation of chromium.

The same result can be obtained with ammonium formate or succinate.

Aluminium and chromium from iron, zinc, manganese, nickel, and cobalt. Mix the solution with a moderate quantity of pure normal potassium tartrate, then with pure caustic potash or soda until the precipitate redissolves, add ammonium sulphide in slight excess and allow to stand. Wash the precipitate with water containing ammonium sulphide. Aluminium and chromium are in the filtrate, the other metals in the precipitate. If iron and chromium are absent, it is sufficient to add the alkaline tartrate, excess of ammonia, ammonium chloride and ammonium sulphide.

Separation of iron and aluminium. The following methods have also been employed for this important separation. (i.) Potassium hydroxide dissolves aluminium hydroxide, but not ferric hydroxide ; the former is reprecipitated from the filtrate by boiling with ammonium chloride or adding successively nitric acid and ammonia ; the iron precipitate is dissolved in acid and reprecipitated by ammonia. (ii.) The two metals are precipitated with ammonia and the weight of the combined oxides determined. The mixture is then digested with strong hydrochloric acid (10 concentrated solution : 1 water) until all the iron has dissolved ; the presence of free chlorine or hydriodic acid assists the solution of the ferric oxide. If alumina predominates, it may be necessary to fuse the mixed oxides with potassium pyrosulphate. The solution is saturated with hydrogen sulphide to reduce the iron to the ferrous condition ; the excess of this sulphide is expelled by carbon dioxide, and the liquid titrated with standard permanganate. The proportion of aluminium is determined by difference. (iii.) Iron and aluminium may also be separated by treating the mixed chlorides with strong hydrochloric acid and ether (equal vols.) ; the aluminium chloride is precipitated, collected, washed with ethereal hydrochloric acid and ignited with mercuric oxide (Gooch and Havens, Amer. J. Sci. 1896, 2, 416). (iv.) The separation of small quantities of aluminium from excess of iron has been successfully effected by the use of phenylhydrazine. The iron is first reduced to the ferrous condition by adding hydrochloric acid and ammonium bisulphite, and the solution almost neutralised with ammonia, a slight excess of phenylhydrazine is then added, and after one hour the aluminium hydroxide is collected and washed with a solution of phenylhydrazine sulphite. In this way

aluminium can be separated from iron, manganese, calcium, and magnesium (Hess and Campbell, J. Amer. Chem. Soc. 1899, 21, 776).

Separation of iron, aluminium, and phosphoric acid. When the total amount of these substances is small, the precipitate obtained by ammonia is ignited and weighed ($A=Fe_2O_3 + Al_2O_3 + P_2O_5$). The precipitate is then fused with sodium carbonate and silica, and the mass extracted with water containing a little ammonium carbonate. The residue containing iron and aluminium is evaporated down with sulphuric acid to dissolve the iron; the solution is reduced with hydrogen sulphide as in the preceding separation, and titrated with permanganate solution. The solution, which contains all the phosphoric acid, is evaporated down with hydrochloric acid to remove silica; the residue taken up with water, and the phosphoric acid precipitated from the filtrate as magnesium ammonium phosphate. From the weight of magnesium pyrophosphate obtained the amount of P_2O_5 is determined, and the Al_2O_3 is obtained by difference. If the total amount of these three substances is large, the original solution may be divided into three aliquot portions, in one of which the phosphoric acid is precipitated as ammonium phosphomolybdate, in the second part the iron is determined volumetrically, and from the third the total precipitate (Fe_2O_3, Al_2O_3, P_2O_5) is obtained (compare Cooksey, Analyst, 1908, 33, 437).

Chromium is readily separated from many metals, *e.g.* aluminium, by conversion into chromate, which is not precipitated by alkalis. This can be done in one of the following ways. (*a*) Make the solution alkaline with caustic potash or soda, saturate with chlorine, and then heat to expel excess of gas, and decompose hypochlorites by heating with ammonia. (*b*) Ammonium persulphate is added to a solution containing chromium, iron, and aluminium. On boiling, the chromium is oxidised to chromate, the acid set free during oxidation being sufficient to keep the iron and aluminium in solution (G. v. Knorre, Zeitsch. anorg. Chem. 1903, 16, 1097). (For the estimation of chromium in chromite and chrome steel, *see Volumetric section.*)

Aluminium from chromium. After chromium has been converted into chromic acid, the aluminium may be precipitated as hydroxide or as phosphate (*v. Determination of metals*). The filtrate is acidified, heated to boiling, and sodium thiosulphate added until the chromium is completely reduced; it can then be estimated as phosphate in the same way as aluminium.

Uranium is separated from the other metals of this group by the solubility of its hydroxide, sulphide, and acid uranates, in ammonium carbonate.

Uranium from iron and aluminium. An acid solution containing ammonium salts is mixed with excess of ammonium carbonate and ammonium sulphide in a closed flask. The precipitate contains ferrous sulphide and aluminium hydroxide; the uranium remains dissolved as the double carbonate $UO_2 \cdot CO_3, 2(NH_4)_2CO_3$. The filtrate is concentrated considerably, acidified with hydrochloric acid, boiled, and the uranium precipitated as ammonium diuranate with ammonia. The precipitate is ignited and weighed as U_3O_8. Or this oxide is heated

with dilute sulphuric acid (1 : 6) at 170° in an inert atmosphere (carbon dioxide); the solution which contains uranyl sulphate (2 mols.) and uranous sulphate (1 mol.), is titrated with standard permanganate solution.

$$1 \text{ c.c. } \tfrac{N}{10}\text{KMnO}_4 = 0.03593\text{U}.$$

Uranium ores are treated in the following way. The mineral (0·5–1·0 gram) is dissolved in nitric acid or *aqua regia*, silica removed by evaporation, the soluble residue extracted with hydrochloric acid, and the metals of the copper group precipitated by hydrogen sulphide. The filtrate is oxidised with potassium chlorate, and treated successively with ammonium phosphate, ammonia (till nearly neutral), and sodium carbonate in excess. The mixture is boiled and sufficient ammonium chloride added to decompose excess of sodium carbonate. The precipitate, which contains the iron, vanadium, &c., is washed with aqueous ammonium carbonate. This salt is removed from the filtrate by boiling alone and with nitric acid. The solution is almost neutralised with ammonia, and to the boiling liquid are added successively microcosmic salt, sodium thiosulphate, acetic acid, and finally ammonium acetate. The precipitate, uranyl ammonium phosphate, is collected, ignited, moistened with nitric acid, again ignited and weighed as $(UO_2)_2P_2O_7$.

Uranium is separated from thorium (and iron) by means of hydroxylamine hydrochloride, which in ammoniacal solution precipitates thorium and ferric hydroxides, leaving the uranium in solution (Jannasch and Schilling, Chem. Zeit. 1905, 29, 248).

Cerium is separated *from other metals* by saturating the solution with sodium sulphate, this salt being added in fine powder. A crystalline double sulphate of cerium and sodium separates, and is washed with a saturated solution of sodium sulphate.

Glucinum is precipitated with aluminium in Group III., and separated from aluminium and the other metals of the group by one of the following methods : (i.) A saturated solution of sodium hydrogen carbonate dissolves out glucinum hydroxide from a precipitate containing aluminium and ferric hydroxides, leaving the latter unaffected (Parsons and Barnes, J. Amer. Chem. Soc. 1906, 28, 1589). (ii.) Aluminium and glucinum chlorides are separated by saturating their solutions with hydrogen chloride in the presence of ether; the former is precipitated, the latter remaining dissolved (Amer. J. Sci. [4] 11, 416). (iii.) The acetates may be separated by the use of hot glacial acetic acid, from which solvent basic glucinum acetate $Gl_4O(CO_2 \cdot CH_3)_6$ separates on cooling (Parsons and Robinson ; cf. also Glassmann, Ber. 1906, 39, 3366; and J. Amer. Chem. Soc. 1895, 17, 688).

Barium carbonate decomposes glucinum chloride, thus separating this metal from those of Group III*b*.

Vanadium is separated from the majority of metallic elements by fusion with sodium carbonate and potassium nitrate; the vanadium dissolves in water as sodium vanadate. Chromium and manganese would also be found in the aqueous extract, but from these metals

vanadium is separated by the addition of ammonium sulphide in excess, when chromium and manganese are precipitated respectively as hydroxide and sulphide leaving vanadium in solution as a thiovanadate (cf. Zeitsch. anorg. Chem. 5, 381; Compt. rend. 1904, 138, 810; and Hillebrand, Amer. J. Sci. [4] 6, 209). From arsenic, vanadium may be separated either by reducing with sulphur dioxide and precipitating arsenious sulphide with hydrogen sulphide or by heating the mixed sulphides in hydrogen chloride at 150°, when the arsenic is volatilised (Field and Smith, J. Amer. Chem. Soc. 1896, 18, 1051).

Vanadium is separated from phosphoric acid by reducing vanadic acid to a hypovanadic salt with sulphur dioxide, and precipitating the phosphorus as phosphomolybdate.

Vanadium and molybdenum are separated by the action of hydrogen sulphide on vanadic and molybdic acids under pressure, molybdenum sulphide being precipitated, or ammonium metavanadate may be precipitated by the action of excess of ammonium chloride (Gibbs, Amer. Chem. J. 1883, 5, 371); the latter method serves to separate vanadium from tungsten.

(For methods of estimating vanadium in iron and steel, see Brearley and Ibbotson, The Analysis of Steel Works Materials; and Blair, The Chemical Analysis of Iron.)

Tungsten is separated from the majority of other elements by fusion with alkali carbonate and extraction of the alkali tungstate with water. This extract, when acidified with nitric acid and evaporated to dryness, yields tungstic acid as a residue insoluble in water. From arsenic and phosphoric acids tungstic acid is separated by the addition of magnesia mixture, which precipitates the arsenic and phosphorus, leaving the tungstate in solution (Gooch, Amer. Chem. J. 1871, 1, 412; and Gibbs, *ibid.* 1885, 7, 337).

The tungsten in wolframite may be estimated by fusing the finely powdered ore (0·5 gram) with 6 parts of fusion mixture in a platinum crucible for half an hour. The fused mass is extracted with boiling water when alkali tungstate passes into solution together with silicate and stannate. The insoluble residue contains iron, manganese, calcium, and magnesium with small amounts of columbic and tantalic acids. The filtrate is evaporated to dryness with excess of nitric acid, and the residue, after heating at 120°, is extracted with dilute ammonium nitrate solution; the residue, which consists of tungstic oxide with silica and stannic oxide, is weighed and then treated with hydrofluoric acid and weighed again. This second residue consists of tungstic oxide and stannic oxide, and the latter is volatilised by heating repeatedly with ammonium chloride until the weight of the final residue (WO_3) is constant.

To remove tin the mixed oxides may be ignited with zinc powder, and the residue, after extraction with hydrochloric acid, is tungsten trioxide (Angenot, Zeitsch. angew. Chem. 19, 140).

(For other separations of tungsten from its usual associates, see J. Amer. Chem. Soc. 1900, 22, 772; Zeitsch. anorg. Chem. 1905, 45, 396; Zeitsch. anal. Chem. 1908, 47, 37; Bull. Soc. Chim. 1908, 13, 892.)

Vol. I.—T.

Columbium and *tantalum* are extracted from columbite or tantalite by fusing the mineral with potassium hydrogen sulphate and extracting the fused mass with hot water and hydrochloric acid. The residue is treated with ammonium sulphide to remove tin, tungsten, and again extracted with hot hydrochloric acid. The final residue is then dissolved in hydrofluoric acid, the filtered solution is treated with potassium carbonate: potassium tantalofluoride separates in acicular crystals and the mother liquor furnishes potassium columbium oxyfluoride, crystallising in plates (compare Weiss and Landecker, Zeitsch. anorg. Chem. 1909, 64, 65; and Chesneau, Compt. rend. 1909, 149, 1132).

Titanium. In addition to the process given under the estimation of titanium, this element may be separated from iron by the following methods: (i.) By adding ammonium sulphide to an alkaline tartrate solution of the two elements, when ferrous sulphide is precipitated (Gooch, Amer. Chem. J. 1885, 7, 283). (ii.) By precipitating titanic acid with phenylhydrazine (J. Amer. Chem. Soc. 1895, 25, 421). Titanium is separated from aluminium by boiling with an alkali acetate and dilute acetic acid, when basic titanium acetate is precipitated.

Titanium and *zirconium* are separated by the following methods: (i.) A solution of the elements in dilute sulphuric and acetic acids is boiled for some time, when titanic acid is precipitated (J. pr. Chem. 1869, 108, 75; Zeitsch. anal. Chem. 9, 388). (ii.) The acid solution is boiled with zinc till the titanium is reduced to titanous salt, the zirconium is then precipitated by the addition of potassium sulphate (Compt. rend. 1863, 57, 298). (iii.) A neutral solution of the nitrates is added drop by drop to a boiling concentrated solution of ammonium salicylate ($1:5H_2O$), the solution boiled for one hour, concentrated, and the precipitated zirconium salicylate collected and washed with ammonium salicylate solution. Titanium salicylate is soluble in hot water and remains in the filtrate (Dittrich and Freund, Zeitsch. anorg. Chem. 1907, 56, 337, 348).

Cerium is precipitated in the aluminium group (III.a), and, together with the other metals of the rare earths, is separated from iron and aluminium by means of oxalic acid or ammonium oxalate. From lanthanum, praseodymium, and neodymium it may be separated by suspending the hydroxides in aqueous caustic potash and passing in chlorine until the liquid is no longer alkaline. The cerium remains precipitated as the yellow hydrated dioxide, whilst the other hydroxides are dissolved (Mosander). Various methods have been proposed similarly based on the oxidation of cerous compounds to the ceric condition (v. Ann. Chem. Pharm. 131, 359; Monatsh. 1884, 5, 508; Ber. 35, 672).

Thorium, together with the rare earths, is separated from the other elements by oxalic acid. The further separation is effected by the following methods:—

(i.) Monazite sand is heated with concentrated sulphuric acid at 180°–200° for 2 to 3 hours, and the product taken up with water, and the rare earths precipitated by the addition of oxalic acid. The precipitated oxalates, after

washing till free from phosphoric acid, are
ignited, and the resulting oxides dissolved in
hydrochloric acid. The excess of acid is ex-
pelled by evaporation at 100°, the residue dis-
solved in water and treated with sodium
thiosulphate. After 12 hours the solution is
boiled for 10 minutes and filtered. The pre-
cipitate contains thorium, but contaminated
with cerium; it is therefore redissolved and
the precipitation repeated until the filtrate gives
no precipitate on boiling with ammonia. At
this stage the precipitate is ignited, fused with
sodium hydrogen sulphate, the product dis-
solved in water, and the thorium finally preci-
pitated with oxalic acid, the precipitate being
ignited and weighed as ThO_2 (Fresenius and
Hintz, Zeitsch. anal. Chem. 35, 543).

(ii.) The mixed oxalates obtained as before
from the monazite sand are decomposed, and
the metals converted into nitrates by repeated
evaporation with nitric acid. The neutral solu-
tion of the nitrates is diluted with aqueous
ammonium nitrate (10 p.c.) warmed to 80°,
and the thorium precipitated as peroxide by the
addition of pure hydrogen peroxide solution.
The precipitate, which contains a trace of
cerium peroxide, is filtered, washed with aqueous
ammonium nitrate, ignited and weighed as
ThO_2 (Benz, Zeitsch. angew. Chem. 1902, 15,
297; compare Chem. Zeit. 1908, 32, 509).

(iii.) Precipitation by organic acids. (α) Fumaric
acid precipitates thorium fumarate in 40 p.c.
alcohol, leaving the other rare earths in solution
(Metzger, J. Amer. Chem. Soc. 1902, 24, 901).
(β) m-Nitrobenzoic acid in aqueous solution
precipitates its thorium salt, the separation
being complete in the presence of aniline.
Under these conditions, cerium, praseodymium,
neodymium, and lanthanum remain in solu-
tion (Kolb and Akele, Zeitsch. angew. Chem.
1905, 18, 92).

(iv.) Boiling with potassium azide in neutral
solution leads to the precipitation of thorium
hydroxide, the salts of the other rare earth
metals being unaffected (Dennis, J. Amer. Chem.
Soc. 1896, 18, 947). Fusion with potassium
hydrogen fluoride separates thorium and cerium
from zirconium, for on extraction with water
containing a little hydrogen fluoride, potassium
zirconofluoride dissolves, leaving behind the
fluorides of thorium and cerium (Chem. News,
1897, 75, 230).

Manganese and *iron* are separated in their
alloys (ferromanganese, &c.) by dissolving the
alloy in hydrochloric acid with a little nitric
acid. After boiling off nitrous fumes, the solu-
tion is filtered and diluted with boiling water
to 600 c.c. Ammonia is added till a faint
turbidity remains, excess of neutral ammonium
acetate is then quickly added, and the solution
boiled. The basic ferric acetate thus precipi-
tated contains some manganese; it is therefore
redissolved and the separation repeated. The
united filtrates are treated with excess of
bromine followed by strong ammonia also in
excess; the liquid is vigorously agitated during
the addition of these reagents, and then heated
slowly to boiling. The precipitate is collected,
washed with boiling water, ignited and weighed
as Mn_3O_4 (compare Riggs, Amer. J. Sci. 43, 135;
Gooch, Zeitsch. anorg. Chem. 1898, 17, 268;
Brearley and Ibbotson, Chem. News, 1902, 82,

209; Zeitsch. anal. Chem. 1904, 43, 382;
Jannasch and Rühl, J. pr. Chem. 1905, 72, 1;
Moore and Miller, J. Amer. Chem. Soc. 1908,
30, 593).

Nickel from cobalt. The solution, which
should contain but little free acid, is mixed with
excess of pure potassium cyanide free from
cyanate (the ordinary cyanide is fused with char-
coal, dissolved in water, filtered, and evaporated
in a silver dish), heated to boiling, and mixed
with a solution of mercuric oxide in mercuric
cyanide. The precipitate, when washed, dried,
and ignited, leaves a residue of nickel oxide
NiO, which is weighed. Cobalt is usually deter-
mined by difference; but if direct estimation
is required, the filtrate from the nickel is eva-
porated to dryness, heated for some time
with strong sulphuric acid, and the cobalt
estimated in the solution.

Nickel can be separated from cobalt and all
the other metals of Groups III. and IV. by pre-
cipitation in ammoniacal or dilute acetic acid
solution with dimethylglyoxime (*see Estimation
of nickel*). If ferric salts are present, they should
be reduced to the ferrous condition, or tartaric
acid is added before rendering the solution alka-
line; the organic acid prevents the co-precipita-
tion of iron, chromium, and aluminium (Brunck,
Zeitsch. angew. Chem. 1907, 20, 1845).

Cobalt from nickel. (i.) In acetic acid solution,
nitroso-β-naphthol precipitates the cobalt as
cobaltic nitroso-β-naphthoxide (Ilinski and
Knorre, Ber. 18, 699). (ii.) Cobaltic hydroxide is
precipitated from a neutral solution of the two
metals by barium carbonate and bromine water
(Taylor, Proc. Manchester Phil. Soc. 1902, 46,
(ii.) 1). (iii.) Small quantities of cobalt can be
detected and estimated in the presence of nickel
by adding to a neutral solution concentrated
aqueous ammonium thiocyanate. On shaking
with amyl alcohol and ether, these organic
solvents extract the double salt $(NH_4)_2Co(CNS)_4$
(blue solution), leaving the nickel in the aqueous
solution (Ber. 1901, 34, 2050 and 3913). Zinc
is also removed with the cobalt.

Cobalt is precipitated as double nitrite on
adding potassium nitrite to an acetic acid solu-
tion of the two metals; the nickel is left in solu-
tion (Fischer, Pogg. Ann. 72, 477; and Funk,
Zeitsch. anal. Chem. 1907, 46, 1).

*Separation of zinc, manganese, nickel, and
cobalt.* The slightly acid solution of the four
metals is treated with sodium carbonate till a
permanent precipitate is formed, which is redis-
solved by a few drops of hydrochloric acid;
then for every 100 c.c. of liquid 15 drops of the
same acid are added, followed by 10 c.c. of 20 p.c.
ammonium thiocyanate; the solution heated to
70° is then saturated with hydrogen sulphide;
the zinc in the precipitate is determined either
as sulphide or oxide. Manganese is separated
from nickel and cobalt by passing hydrogen
sulphide into a solution of their salts in acetic
acid containing excess of ammonium acetate,
when nickel and cobalt are precipitated as
sulphides; the filtrate may, however, still con-
tain small amounts of these metals. The solu-
tion is concentrated, treated with ammonium
sulphide, and then with acetic acid. A further
precipitate of nickel and cobalt sulphides is
thus obtained (*v.* Treadwell and Kramers,
Zeitsch. anorg. Chem. 1901, 26, 184; compare

J. Soc. Chem. Ind. 1905, 24, 228; Bull. Soc. Chim. 1908, (iv.) 3, 114).

Zinc from nickel and cobalt. Add excess of pure potassium cyanide and precipitate the zinc with sodium sulphide.

GROUP IV.—The metals of this group are separated from those of the following group by precipitation with ammonium carbonate (*v. General methods of estimation*). The liquid is first made alkaline with ammonia and afterwards heated to boiling to ensure complete precipitation.

Barium from calcium and strontium. The dilute neutral or feebly acid solution is mixed with excess of freshly prepared hydrofluosilicic acid and one-third its volume of 95 p.c. alcohol allowed to stand twelve hours, collected on a weighed filter, washed with a mixture of equal parts of water and alcohol, and dried at 100°. Calcium and strontium are not precipitated.

Barium from strontium. Ammonium bichromate and ammonium acetate are added alternately to a solution of barium and strontium salts containing ammonium acetate. After three hours the precipitate, $BaCrO_4$, is washed with ammonium acetate solution, dried at 180°, and weighed (Kahan, Analyst, 1908, 33, 12; *v.* Zeitsch. anal. Chem. 1905, 44, 742; J. Amer. Chem. Soc. 1908, 30, 1827).

Barium and strontium from calcium. The solution is mixed with a concentrated solution of ammonium sulphate, using 50 parts of the latter salt for one part of the mixed salts, heated to boiling with addition of a small quantity of ammonia, and the precipitate washed with water containing ammonium sulphate. The filtrate contains the calcium, which can be precipitated by ammonium oxalate.

Calcium from strontium. Convert the metals into nitrates, evaporate to dryness, and extract with a mixture of equal volumes of alcohol and ether, which dissolves calcium nitrate but not strontium nitrate.

Calcium from strontium and barium. The nitrates are dried at 140° and extracted with amyl alcohol, which dissolves out the calcium salt, leaving the other two undissolved (Browning, Amer. J. Sci. 43, 50, 314).

Calcium from magnesium. The calcium is precipitated by ammonium oxalate (*v. Determination of metals*), adding sufficient of this salt to convert both metals into oxalates, since calcium oxalate is appreciably soluble in a solution of magnesium chloride. In very accurate separations the precipitate should be filtered off, redissolved in hydrochloric acid, and reprecipitated by adding excess of ammonia and a small quantity of ammonium oxalate (*cf.* Richards, Zeitsch. anorg. Chem. 1901, 28, 71; Zeitsch. angew. Chem. 1908, 21, 592; J. Amer. Chem. Soc. 1909, 31, 917).

GROUP V.—*Magnesium from alkalis.* The magnesium is precipitated with ammonium phosphate in the usual way, the filtrate evaporated to dryness, heated to expel ammonium salts, the residue evaporated two or three times with strong nitric acid to remove hydrochloric acid, and the phosphoric acid removed by stannic oxide (*v. Phosphoric acid from metals; v.* Gibbs, Amer. J. Sci. [3] 5, 114; Neubauer, Zeitsch. angew. Chem. 1896, 9, 439; Gooch, Zeitsch. anorg. Chem. 1899, 20, 121).

In solutions free from ammonium salts, the magnesium can be precipitated as magnesium hydroxide by the addition of aqueous barium hydroxide. The excess of barium is removed by ammonium carbonate and the alkalis are determined in the filtrate. Magnesium chloride is also separated from the alkali chlorides by ignition with mercuric oxide, when mercuric chloride and the excess of oxide volatilise, leaving magnesia, from which the soluble alkali chlorides are readily separated.

Alkalis from magnesium. (a) The solution is made distinctly alkaline with pure milk of lime (calcium hydroxide suspended in water) and boiled for some time. care being taken that it remains alkaline. The liquid is filtered, made alkaline with ammonia, and the calcium precipitated by adding ammonium carbonate and a small quantity of ammonium oxalate. The filtrate is acidified with hydrochloric acid and evaporated in a weighed platinum dish, heated to expel ammonium salts, and the alkaline chlorides weighed. They should dissolve completely in water and should give no precipitate when mixed with ammonium carbonate and allowed to stand for some time. If any calcium is present, it must be removed by repeating the treatment with ammonium carbonate and oxalate.

(b) The solution, which must contain only potassium, sodium, and magnesium, is mixed with excess of oxalic acid, evaporated to dryness, and the oxalic acid expelled by heating carefully over a lamp until white fumes cease to come off. The residue is treated with water, when potassium and sodium dissolve as carbonates, whilst magnesium oxide remains undissolved.

Alkalis from silicates. (a) The finely powdered silicate (1 gram) is mixed intimately with an equal weight of ammonium chloride and eight parts of dense granular calcium carbonate, and heated to redness for half an hour. The product is boiled with water in a platinum or silver dish for two hours, care being taken to make up the loss by evaporation, the liquid is filtered and the residue well washed with hot water. The filtrate, which contains calcium and the alkalis, is treated in the manner just described. In this method of decomposition, which is due to J. Lawrence Smith, the silicate is decomposed by the calcium oxide, which is dissolved by the fused calcium chloride formed by the action of the ammonium chloride on the calcium carbonate.

(b) The silicate is treated in a platinum dish with excess of sulphuric and hydrofluoric acids, and the mixture evaporated on the water-bath until the mineral is entirely decomposed. The temperature is then raised to drive off the greater part of the sulphuric acid, and the cooled residue extracted with water. The sulphates are converted into chlorides by barium chloride, the metals of Groups III. and IV. precipitated by ammonia and ammonium carbonate, the magnesium removed by barium hydroxide, and the excess of this reagent eliminated by ammonia and ammonium carbonate. The alkali chlorides remaining in the final filtrate are estimated as indicated in the following section. Certain native silicates of the andalusite group are not decomposed completely by this treatment with hydrofluoric acid; these minerals

may, however, be broken up by ignition with ammonium fluoride.

(c) The alkali and other metals contained in a refractory silicate may be separated by heating the mineral with lead carbonate. The product is extracted with nitric acid; the lead removed as chloride and sulphide, and the metals in solution dealt with in the customary manner (Jannasch, Zeitsch. anorg. Chem. 1895, 8, 364).

(d) Silicates of different types are decomposed by fusion with boric anhydride followed by extraction with methyl alcoholic hydrogen chloride and evaporation to remove the boric acid as volatile methyl borate (Ber. 1895, 28, 2822; Zeitsch. anorg. Chem. 1896, 12, 208).

Potassium from sodium. The metals are converted into chlorides, which are evaporated to dryness and weighed together after drying at 150°. The salts are dissolved in water, mixed with platinic chloride in sufficient quantity to convert both into platinichlorides, and evaporated nearly but not quite to dryness. The residue is then treated with alcohol, which dissolves the sodium but not the potassium salt (*v. Potassium*). If the mixture is evaporated to complete dryness and heated so that the sodium platinichloride becomes anhydrous, it dissolves with difficulty in alcohol. Under some conditions reversion takes place and sodium chloride separates in white crystals insoluble in alcohol. In this case the alcohol is very carefully evaporated and the residue again treated with platinic chloride.

In order to separate small quantities of potassium from large quantities of sodium, advantage may be taken of the fact that potassium chloride is more soluble than sodium chloride in strong hydrochloric acid (Zeitsch. analyt. Chem. 1880, 156). The dry mixed chlorides are thoroughly moistened with concentrated hydrochloric acid: 2 c.c. of the acid is then added, and the salt thoroughly crushed and stirred with a glass rod. After standing for a few minutes the acid is poured off into a small dish. Ten repetitions of this treatment, using 2 c.c. of acid each time, will suffice to remove all potassium, whilst the greater part of the sodium chloride is not dissolved. The acid solution is evaporated to dryness and the potassium determined as platinichloride (Chem. Soc. Trans. 39, 506). By adopting this plan much less platinic chloride is required, and the separation is much more accurate.

Lithium from sodium and potassium. When a lithia-containing silicate (*e.g.* lepidolite) is broken up by one of the preceding processes the precipitable metals of Groups I.–IV. are first removed and the alkali metals converted into chlorides. The combined chlorides are dried and weighed; potassium is estimated in one portion, and in a second portion the lithium is estimated by extracting the chlorides with amyl alcohol or with ether-alcohol saturated with hydrogen chloride. Anhydrous lithium chloride is soluble in these media, whereas sodium and potassium chlorides are practically insoluble therein. Lithium chloride has also been separated from the chlorides of the other alkali metals and barium by dissolving it in boiling pyridine, in which the others are insoluble (Kahlenberg and Krauskopf, J. Amer.

Chem. Soc. 1908, 30, 1104). (For the separation of lithium as phosphate and fluoride, *see* Ann. Chim. Phys. 98, 193; Frdl. 29, 332, and Analyst, 16, 209.)

Rubidium and *cæsium* are separated from each other and from potassium by taking advantage of the difference in the solubility of their platinichlorides. Rubidium hydrogen tartrate is more than nine times less soluble than the cæsium salt. Cæsium carbonate alone of the alkali carbonates is soluble in alcohol. Cæsium gives rise to a series of sparingly soluble perhalides and yields double chlorides with lead and antimony chlorides (*v.* Wells, Amer. J. Sci. 43, [3] 17; and Amer. Chem. J. 1901, 26, 265).

Ammonium salts can be removed from a solution in two ways: (1) By evaporating to dryness and carefully heating over a lamp until all fumes cease to come off. (2) By concentrating the solution and heating for some time with excess of strong nitric acid. When evolution of oxides of nitrogen ceases, the liquid is evaporated to complete dryness and the nitrates converted into chlorides by repeated treatment with hydrochloric acid if necessary.

B. *The Estimation of Acid Radicles.*

Bromine from chlorine. (a) The two elements are precipitated by excess of silver nitrate and weighed together. The filter ash is removed, the precipitate cautiously heated to fusion, and a portion poured into a weighed porcelain boat. The boat is again weighed, heated to fusion in a current of dry chlorine in a glass tube until all bromine is expelled, and the silver chloride formed is weighed. It is advisable to heat in chlorine for a further period of ten minutes and weigh again. The loss of weight multiplied by 4.223 gives the amount of silver bromide in the weight of precipitate treated with chlorine, from which the quantity in the whole precipitate is readily calculated (*v. Indirect methods of determination*).

This method gives accurate results if the proportion of bromine is not too small. When a small quantity of bromine is mixed with a large quantity of chlorine, the former may be concentrated by taking advantage of the fact that if a limited quantity of silver nitrate is added, the precipitate will contain all the bromine, but only a portion of the chlorine. In one portion of the substance the two elements are determined together by complete precipitation. Another portion in somewhat dilute solution is mixed with a quantity of silver nitrate insufficient for complete precipitation, and allowed to stand in the cold for some time with repeated agitation. The precipitate is collected, washed, and weighed, and the proportion of bromine determined in the manner already described. The quantity of silver nitrate which should be used depends upon the relative proportions of chlorine and bromine. If one part of bromine is present for every 1000 parts of chlorine, one-fifth or one-sixth of the silver necessary for complete precipitation should be used; if one part to 10,000, only one-tenth; if one part to 100,000, only one-sixtieth (Fehling).

(b) The solution of the two halides heated at 70°–80° is treated with ammonium persulphate, and the liberated bromine volatilised in a current of air, collected in sulphurous acid, and

estimated as silver bromide (Engel, Compt. rend. 1894, 118, 1263).

Iodine is separated from chlorine in exactly the same way as bromine from chlorine. The loss of weight on treating with chlorine, multiplied by 2·569, gives the weight of silver iodide in the portion of precipitate taken.

Iodine from chlorine or bromine. The solution is slightly acidified with hydrochloric acid, mixed with palladious chloride until precipitation is complete, and allowed to stand in a warm place for twenty-four or forty-eight hours. The precipitate of palladious iodide PdI_2 is collected on a weighed filter, washed with warm water, and dried at 100°, or is reduced by heating in hydrogen and the metal weighed.

Iodine can also be liberated by nitrous acid and estimated volumetrically (*v. Volumetric methods*).

Bromine, chlorine, and iodine from one another. (*a*) The three elements are precipitated and weighed together in one part of the solution. In another part the iodine is separated as palladious iodide by palladious chloride, or better, nitrate; the excess of palladium is removed by hydrogen sulphide and excess of the latter by ferric sulphate; and the chlorine and bromine in the filtrate are precipitated completely or fractionally and the bromine determined in the manner previously described. The chlorine is estimated by difference.

(*b*) A direct method of estimating the three halogens in a mixture of their soluble salts has been investigated by Jannasch and his collaborators. The process in its present stage of development gives a sharp separation of chlorine and iodine, but the results for bromine are rather low. The mixture dissolved in 25 c.c. of water is heated to boiling with acetic acid and hydrogen peroxide, and the liberated iodine expelled by a current of carbon dioxide. The bromine is then liberated by adding excess of hydrogen peroxide and moderately strong sulphuric acid (5 : 3). The iodine is collected in an ammoniacal solution of hydrazine sulphate and the bromine in alkaline hydrazine sulphate. After acidifying with nitric acid, the iodine and bromine are precipitated as silver salts, and the chlorine left in the distilling flask is similarly precipitated (Ber. 1906, 39, 196, 3655; J. pr. Chem. 1908, 78, 29; Zeitsch. anorg. Chem. 1, 144 and 245). (For other processes for separating the halogens, *see Volumetric section*; and Monatsh. 13, 1; Chem. Soc. Trans. 1893, 63, 1051; Compt. rend. 1898, 126, 187; Ber. 1899, 32, 3615.)

Several indirect methods of estimating these three elements in a mixture have been proposed. They are based on the methods given, together with the fact that the radicles may be precipitated exactly by a standard solution of silver nitrate and the precipitate weighed, the proportion of silver and halides in the precipitate being thus determined (*v. Fresenius, Quantitative Analysis, sect. 5*).

Indirect Methods of Determination. This estimation of two or three halogens in a mixture furnishes a good example of indirect methods of analysis, which are adopted in those cases where the separation of two or more constituents is either impossible or inconvenient.

The calculation of the relative proportions of these constituents becomes possible when one can obtain as many independent relationships as there are radicles to be determined. The estimation of chlorine and bromine (*a*) is a case in point. The loss of weight due to the replacement of Br.(79·92) by Cl(35·46) is proportional to the amount of bromine present. Let $w =$ loss of weight. Now

$$\frac{Cl}{Br} = \frac{35·46}{79·92} \text{ and hence } Br - \frac{35·46}{79·92}Br = w;$$

or $Br = 1·797 \ w$: *i.e.* the loss of weight multiplied by 1·797 gives the quantity of bromine present.

Similarly, the halogens in a mixture of soluble chloride, bromide, and iodide can be calculated from the following data : (i.) the amount of iodine present, set free by nitrous acid or hydrogen peroxide and acetic acid ; (ii.) the total weight of mixed silver halides obtained from a known amount of mixture ; (iii.) the silver required for the complete precipitation of the three halogens ; this is obtained volumetrically. The indirect method can also be applied to the estimation of sodium and potassium contained in the mixed chlorides from a silicate analysis (*v. supra*). The data required are : (i.) the weight A of mixed chlorides ; (ii.) the weight B of chlorine therein contained, this amount being determined either gravimetrically or volumetrically. Let x and y be the amounts of potassium and sodium respectively, then these quantities are readily calculated from the following equations, where Cl, K, and Na represent the atomic weights of these elements.

$$x + y = A - B$$
$$\frac{Cl}{K}x + \frac{Cl}{Na}y = B$$

These indirect methods give useful results only when the atomic or molecular weights of the two radicles differ considerably, and when the quantities present are approximately equal. Moreover, the results are affected to a considerable extent by comparatively small experimental errors.

Cyanide from chloride. Silver nitrate is added in excess to an approximately 2 p.c. solution of soluble cyanide and chloride. An excess of normal nitric acid is now added, and the mixture containing the freshly precipitated silver salts is distilled, when hydrocyanic acid is expelled quantitatively and estimated in the distillate by precipitation as silver cyanide with acidified silver nitrate, drying this precipitate at 110°, and weighing in a Gooch crucible or on a tared filter paper (Plimmer, Chem. Soc. Trans. 1904, 85, 12 ; compare also Richards and Singer, Amer. Chem. J. 1902, 27, 205).

Phosphoric acid from metals. (*a*) The nitric acid solution, as free as possible from hydrochloric acid, and free from silicic and arsenic acids, is mixed with excess of a solution of ammonium molybdate in nitric acid, heated gently for a few minutes, and filtered after standing for a short time. The precipitate is washed with dilute nitric acid, dissolved in ammonia, and the phosphoric acid precipitated by magnesia mixture. This method is more especially applicable when the quantity of phosphoric acid is relatively small. To prepare ammonium

molybdate solution, 25 grams of the salt is dissolved in 100 c.c. of dilute ammonia, and the solution poured gradually with constant and vigorous agitation into 500 c.c. of a mixture of 3 vols. strong nitric acid and 1 vol. water. The liquid is heated at 50° for some time and the clear solution drawn off.

(b) By stannic oxide. The nitric acid solution is concentrated, mixed with fuming nitric acid boiling at 86°, heated gently, and granulated tin added gradually in quantity not less than four times the amount of phosphoric acid present. The stannic oxide produced forms an insoluble compound with the phosphoric acid. This is filtered off, washed with hot water, dissolved in caustic potash, the solution saturated with hydrogen sulphide, acidified with acetic acid, and the stannic sulphide removed. The filtrate is concentrated, any stannic sulphide which separates subsequently is removed, and the phosphoric acid is estimated in the usual way. The original filtrate from the stannic oxide contains the metals previously combined with the phosphoric acid.

(c) The nearly neutral solution is mixed with silver nitrate and digested for some time with excess of silver carbonate. The phosphoric acid separates as silver phosphate, the metals remain in solution with the excess of silver nitrate. The silver is removed by hydrochloric acid.

(d) When the phosphoric acid is combined with metals which form phosphates insoluble in water but soluble in acetic acid, the solution is nearly neutralised, mixed with sodium or ammonium acetate, and a slight excess of ferric chloride containing a known weight of iron added. The liquid is heated to boiling, the mixture of ferric phosphate and basic acetate washed with hot water, dried, and heated in a platinum crucible until the weight is constant. The weight of the precipitate *minus* the known weight of the ferric oxide gives the phosphoric anhydride P_2O_5. The precipitate may be moistened with nitric acid before the final ignition.

Phosphoric acid in silicates. In the analysis of silicates (*v. supra*) the phosphoric acid is found together with iron and aluminium in the precipitate produced by ammonia in the filtrate from the silica. This mixture is analysed in accordance with the method indicated under the separations of metals (Group III.).

Phosphorus and silicon in iron and steel. The iron or steel borings are dissolved in nitric acid ($1HNO_3$ sp.gr. $1\cdot4:1H_2O$); the solution evaporated to dryness, and the residue ignited carefully until all the ferric nitrate is converted into ferric oxide. The ignited residue is dissolved in concentrated hydrochloric acid heated nearly to boiling, when the ferric oxide and phosphate pass into solution, leaving insoluble silica. The solution is evaporated to dryness, moistened with strong hydrochloric acid, and taken up with water; the silica is collected, ignited, and weighed, its purity being tested by treatment with hydrofluoric and sulphuric acids. The phosphoric acid in the filtrate is estimated by either of the following methods.

(a) The ferric solution, diluted and almost neutralised with ammonia, is reduced with sulphurous acid or sodium sulphite. Hydrochloric acid is added and the excess of sulphur dioxide

expelled by boiling. A small portion of the ferrous iron is now reoxidised with a few drops of bromine water. Ammonia is added carefully till a brown precipitate is formed which becomes green on stirring. Acetic acid is added ill the precipitate either dissolves or becomes whiter, and the solution then heated to boiling. The precipitate, which contains all the phosphorus as ferric phosphate mixed with basic ferric acetate, is dissolved in hydrochloric acid, the solution evaporated nearly to dryness, excess of citric acid added, and then magnesia mixture and ammonia. The magnesium ammonium phosphate is redissolved in hydrochloric acid and reprecipitated in the presence of citric acid to remove a small amount of iron, and ignited and weighed as $Mg_2P_2O_7$.

(b) The filtrate from the silica is evaporated to dryness, the residue dissolved in dilute nitric acid, ammonium nitrate added, and the solution heating to boiling. A boiling solution of ammonium molybdate is then added to phosphate solution, when ammonium phosphomolybdate is precipitated quantitatively. This precipitate is redissolved in ammonia to which ammonium nitrate and ammonium molybdate are added, and reprecipitated by adding hot nitric acid to the boiling solution. The compound is now pure, and is collected, washed with water containing ammonium nitrate and nitric acid, and either dried at 160°–180° or gently ignited. In the former case it is weighed as $(NH_4)_3PO_4$, $12MoO_3$ (containing 3·782 p.c. P_2O_5) or in the latter as $P_2O_5,24MoO_3$ (containing 3·946 p.c. P_2O_5) (*v.* Ber. 1878, 11, 1640; Zeitsch. anorg. Chem. 1893, 32, 144; Amer. Chem. J. 34, 204; Analyst, 1909, 34, 392; Chem. Zeit. 21, 442). Separation of phosphoric and titanic acids (*v.* J. Soc. Chem. Ind. 1895, 14, 443). Estimation of phosphorus in phosphor-bronze (*v.* J. Amer. Chem. Soc. 1897, 19, 396) in phosphor-tin (J. Soc. Chem. Ind. 1908, 27, 427).

Silicic acid from titanic acid. The silica and titanium dioxide are weighed together, the mixture fused with a somewhat large quantity of potassium hydrogen sulphate, and the cooled mass extracted with water. Silica is left undissolved, titanic oxide dissolves, and can be precipitated from the filtrate by ebullition (*v. Titanium*).

Sulphides. If the sulphides are decomposable by hydrochloric acid, the hydrogen sulphide is absorbed in hydrochloric acid containing bromine (*v. Determination of metals*). Insoluble sulphides are decomposed by gently heating with *aqua regia* or with hydrochloric acid and bromine, and the sulphuric acid estimated in the solution. The latter method gives the total sulphur.

Sulphur in coal and coke. The finely powdered material (1 gram) is mixed intimately with 1 gram of calcined magnesia and 0·5 gram of sodium carbonate, and ignited to dull redness in an open platinum crucible for 1 hour, the mixture being stirred every five minutes with a platinum wire. The mixture is then heated strongly for 10 minutes with 1 gram of ammonium nitrate. The residue is extracted with water and the sulphate determined in the usual way (Eschka). The sulphur may also be determined by heating the coal with sodium or potassium carbonate (4 parts) alone, and extracting

the residue with hydrochloric acid and a few drops of bromine (Nakamura). (Compare also Zeitsch. angew. Chem. 1905, 18, 1560; Chem. Zeit. 1908, 32, 349; J. Russ. Chem. Soc. 1902, 34, 457.)

Sulphur in pyrites. The pyrites is oxidised either by fusion with sodium peroxide and sodium carbonate or by oxidation with nitric acid and bromine. These processes convert the sulphur to sulphate, which is estimated in the usual way (*v.* J. pr. Chem. 1892, [2] 45, 103; Zeitsch. anorg. Chem. 6, 303, *l.c.* 1896, 12, 129; J. Soc. Chem. Ind. 1905, 24, 7; Chem. News, 1906, 93, 213).

Sulphuric acid from all other acids except hydrofluosilicic by precipitation with barium chloride in presence of hydrochloric acid.

Sulphuric acid from hydrofluosilicic acid. The solution is mixed with excess of potassium chloride and an equal volume of strong alcohol, filtered through a weighed filter, and the precipitate of potassium silicofluoride (K_2SiF_6), washed with a mixture of equal volumes of alcohol and water, and dried at 100°. The sulphuric acid in the filtrate is estimated in the usual way after evaporation of the alcohol.

Titanic acid from silicic acid (*v. Silicic acid from titanic acid*).

Boric acid. The borates of the alkali and alkaline earth metals, when heated with pure methyl alcohol (free from acetone) and acetic acid, evolve all the boron present in the form of methyl borate (b.p. 65°). This liquid, when added to moist lime, is completely hydrolysed and the boric acid set free combines with the calcium oxide forming calcium borate. The decomposition is effected in a small retort fitted with a tap funnel for introducing further quantities of methyl alcohol. The retort is connected with a water condenser and a conical flask containing a weighed amount of quicklime. This lime is carefully slaked before the distillation, and the methyl borate dropping into the conical flask is decomposed and the boric acid taken up by the lime. The contents of the receiver are rinsed into a platinum dish, and the methyl alcohol evaporated at as low a temperature as possible. The residue is cautiously ignited to destroy calcium acetate, and the increase in weight of the lime represents the amount of boric anhydride B_2O_3 obtained from the borate. Instead of lime, aqueous ammonium carbonate may be used in the receiver, and the liquid poured on to slaked lime (from a known weight of quicklime) contained in a platinum dish (Zeitsch. anal. Chem. 1887, 26, 18, 364).

VOLUMETRIC METHODS.

In volumetric analysis the proportion of a substance is ascertained, not by separation and weighing, but by determining the exact volume of a reagent solution of known concentration required to produce some particular reaction, such as neutralisation, oxidation, or precipitation. The termination of the reaction is indicated by some end-reaction, which is usually a production, destruction, or change of colour, the formation of a permanent precipitate or the cessation of the formation of a precipitate. In determining the strength of caustic soda, for example, it is coloured yellow with methyl orange, and a dilute solution of sulphuric acid

of known strength is added gradually until the yellow colour of the methyl orange just changes to red, thus indicating the point of neutralisation. The volume of acid required is noted; the weight of sulphuric acid which it contains, and hence the weight of soda which it will neutralise, is known, and thus the proportion of soda in the substance is determined.

In order that a reaction may serve as the basis of a volumetric process, it must be rapid, simple, and definite, and not complicated by secondary reactions. It should remain constant through considerable variations in conditions, and should not, for example, be materially affected by the degree of concentration of the solution. A final reaction should be rapid, perfectly decisive, and should only require a slight excess of the reagent for its production. In many cases a third substance is employed to indicate the completion of the reaction, and is termed an *indicator.* It is an *internal indicator* if it is added to the bulk of the liquid, an *external indicator* if drops of the liquid are removed and brought in contact with it.

The execution of volumetric processes involves the possession of accurately graduated instruments of three kinds, viz. flasks, pipettes, and burettes. The flasks should be fitted with well-ground stoppers, and should have somewhat long necks, the graduation being not higher than the middle of the neck, in order that there may be sufficient empty space for efficient agitation. Flasks holding respectively 1000 c.c., 500 c.c., 250 c.c., and 100 c.c., are used. Each flask should have two graduation marks, viz. the *containing mark,* indicating the point to which the flask must be filled in order that it may then contain the particular volume of liquid, and the *delivery mark* or point to which the flask must be filled in order that it may deliver the given volume of liquid when emptied by draining. A pipette is usually a cylindrical bulb terminating at each end in a tube, the lower of which is drawn out to a jet, whilst the end of the upper tube is slightly contracted so that it may be readily closed by the forefinger and the flow of liquid regulated or stopped altogether. Usually a pipette has only a *delivery* mark, but occasionally they are graduated throughout their whole length, and then take the form of a somewhat wide tube contracted to a jet at the bottom and terminating in a narrower tube at the top. Pipettes of 100 c.c., 50 c.c., 25 c.c., 10 c.c., and 5 c.c. capacity are most generally useful. A burette is a long tube of uniform bore, 12 to 15 mm. in diameter, graduated in cubic centimetres and tenths or fifths. A convenient capacity is 50 c.c. It is open at the top and contracted at the lower end, to which a glass jet is attached by means of a piece of narrow indiarubber tubing. This tubing is nipped by a spring pinchcock, which is opened by the pressure of the fingers, the flow of liquid being thus regulated. A better plan is to insert in the indiarubber tubing a short piece of glass rod the diameter of which is just sufficient to prevent the flow of liquid when the tubing remains circular. If, however, the tubing is squeezed out laterally by the pressure of the thumb and fore finger (Fig. 9), a channel

1   **2**

FIG. 9.

is made through which the liquid can pass, and by increasing or reducing the pressure, the flow of liquid can be regulated to a nicety. Certain reagents act upon indiarubber, and for these a burette with a glass stopcock should be used. This form is, in fact, the most convenient for all purposes. The stopcock may be prevented from sticking by a little vaseline or paraffin, and from slipping out by a small india-rubber ring passed over the tap and round the burette tube. Sometimes the tube carrying the stopcock is not in the same line with the burette, but is bent twice at right angles, so that the burette jet, although still vertical, is one or two inches in advance of the burette itself. This form is useful when titrating hot liquids, since the risk of heating the burette and its contents is reduced. An alternative method is to have the top of an ordinary burette funnel-shaped, which admits of the burette being slung in a stand by the funnel without other support, so that it can be tilted from the vertical when titrating hot solutions.

When a burette is in use, it is important that it should be supported in a vertical position. This can be done by means of a clamp attached to a stand similar to a retort stand. A useful and easily constructed burette stand is described in J. Amer. Chem. Soc. 1905, 27, 1442.

When several different solutions are being used continually, it is convenient to have the series of burettes attached to a revolving stand, so that each may be brought round to the front when required. Short test-tubes inverted over the tops of burettes serve to keep out dust.

Standard solutions should be kept in well-stoppered bottles in a cool place protected from bright light. When many determinations of the same kind have to be made, it is convenient to keep the reservoir of standard solution attached to the burette to facilitate the filling of the latter. A glass T-piece is introduced between the graduated part of the burette and the stopcock or pinchcock, and is attached by means of an indiarubber tube to a tubulus at the bottom of the bottle which contains the standard solution and stands on a shelf above the burette. If this bottle has no tubulus, a glass tube bent twice at right angles, with one limb reaching to the bottom of the bottle and the other connected with the burette, is fitted into the neck of the bottle by means of a cork, and is kept always full, so that it acts as a siphon. There must, of course, be an entrance for air as the liquid flows from the bottle. The flow of liquid into the burette is regulated by a pinchcock on the indiarubber tube. If the standard solution acts upon indiarubber, all these connections must be constructed of glass tubing. Burettes may now be obtained fitted with Greiner and Friedrich's three-way taps (compare Fig. 12); these are readily connected to reservoirs and filled from the bottom. Filling the burette from the bottom avoids the formation of air-bubbles, but it can also be filled from the top if the tube from the stock bottle is bent slightly so that the liquid flows down the side of the burette. A convenient form of apparatus for this method, which is the only one available with an ordinary tap burette without a side-tube attachment, is described in Chem. News, 1906, 93, 71. When the standard solution alters if exposed to air, the surface of the

liquid may be covered with a layer of rectified paraffin of moderately high boiling-point, or the neck of the bottle may be provided with a cork carrying a tube containing caustic potash, or alkaline pyrogallate, through which all air entering the bottle has to pass. A still better plan is to fill the upper part of the stock bottle with carbon dioxide, or, if the nature of the solution permits, with coal gas, and connect it by means of a cork and tube with a self-acting carbon dioxide apparatus or the ordinary gas supply. When solution is withdrawn, carbon dioxide or coal gas enters. The burette should be kept permanently attached to the reservoir as just described, and the top end of the burette also put into communication with the inert gas supply.

Graduation of the instruments.—Accurate calibration of the measuring vessels is of course necessary if correct results are to be obtained, and it is never advisable to trust the makers' graduations. All the instruments should be checked before being taken into use. Although it is sufficient for most purposes if the relative volumes of the vessels are correct, they should nevertheless be graduated in true cubic centi-metres. With gas-volumetric apparatus this procedure is essential. If the calibration is performed at a temperature of 18°–20°, variations from the true volume resulting from the expansion of the glass are so small for the intervals of temperature through which the laboratory is likely to vary, that they may be neglected.

The vessels are checked by ascertaining the weight of distilled water at a known temperature which they will contain or deliver as the case may be. A large beaker of distilled water is placed in the balance room, and left for some hours till its temperature has become constant. The vessels to be calibrated are thoroughly cleansed by successive treatments with concentrated caustic potash, distilled water, and a warm solution of chromic acid in concentrated sulphuric acid, and then rinsed well with distilled water. The flasks are then dried. A narrow strip of paper is attached vertically to the neck of the litre flask near the mark, the flask placed on one pan of a large balance capable of responding to 0·05 gram, and counterpoised. Weights corresponding with the weight of water which at the temperature of the supply in use will occupy 1000 c.c., are then placed in the pan; the flask is filled nearly to the mark with water, and water is gradually added until flask and weights are in equilibrium. Any water adhering to the inside of the neck of the flask above the mark must be removed by means of filter paper. If the mark on the neck of the flask is thus found to be in error, a pencil mark is made on the strip of paper at the point corresponding with the lower edge of the meniscus, the glass above and below is evenly coated with a thin film of wax, and a horizontal ring is scratched through by means of a needle precisely on a level with the pencil mark. The ring is covered with a small piece of filter paper, which is moistened with hydrofluoric acid, care being taken to remove air-bubbles. After a few minutes the acid is washed off and the wax removed, when a new mark will be found etched into the glass.

In calibrating volumes by determining weights of water, it is necessary to reduce the

weight to vacuum standard, and then divide the result by the density of the water in order to obtain accurately the volume in true cubic centimetres. This calculation can be avoided by making use of the following table :—

$t°$	0°	1°	2°	3°	4°	5°
x	1·19	1·13	1·09	1·07	1·06	1·07

$t°$	6°	7°	8°	9°	10°	11°
x	1·09	1·13	1·18	1·25	1·33	1·43

$t°$	12°	13°	14°	15°	16°	17°
x	1·53	1·65	1·78	1·93	2·09	2·25

$t°$	18°	19°	20°	21°	22°	23°
x	2·43	2·62	2·82	3·03	3·26	3·49

24°	25°	26°	27°	28°	29°	30°
3·73	3·98	4·24	4·52	4·80	5·08	5·38

x is the quantity to be subtracted from 1000 to obtain the apparent weight (in air, when brass weights are employed) of 1000 c.c. of water at the temperature t. For example, at 18° the apparent weight of 1000 c.c. is $1000 - 2·43 = 997·57$ grams.

The litre flask having been graduated to contain, it should now be graduated to deliver. The full flask is carefully emptied and allowed to drain for a definite time—say thirty seconds—again counterpoised with the water adhering to the inside, and again filled with a further 1000 c.c. of water in the manner previously described. The other flasks are graduated in the same way, subtracting only $\frac{1}{2}x$ from 500 grams in the case of the 500 c.c. flask, $\frac{1}{4}x$ for 250 grams for the 250 c.c. flask and so on.

The quantity of liquid which a pipette will deliver depends to some extent on the manner in which it is emptied. A small quantity of liquid always remains in the jet, and this should not be blown out. The best plan is to allow the pipette to empty itself whilst held vertically, and then to let it drain for twenty seconds with the point of the pipette just touching the side of the receiving vessel; but the method of emptying employed in the calibration must be adhered to in its subsequent use.

To test the accuracy with which a pipette has been graduated, it is filled to the mark with distilled water at an observed temperature, the contents delivered into a light, tared, stoppered flask, and accurately weighed. The operation is repeated several times, and from the mean result the true volume is calculated by using the table previously given; for it is clear that $1 - \frac{x}{1000}$ denotes the apparent weight of 1 c.c. of water at $t°$, or $1 + \frac{x}{1000}$ equals the volume at $t°$ occupied by 1 gram of water weighed in air with brass weights. If the error in graduation is greater than can be allowed, another mark must be made; its position may be found by repeated trials, a strip of paper being pasted along the stem, and the volumes corresponding to various pencil marks being found as above. The new mark is then etched in with hydrofluoric acid.

A convenient method for directly calibrating pipettes is described by Thorpe (Quantitative Analysis). The pipette is suspended from one arm of a balance by means of a clip, so as to hang perpendicularly and pass through a hole in the bottom of the balance case or of a specially constructed table. A suitable clip (Fig. 10) consists of a stout brass wire frame carrying two clips of sheet brass closed by sliding collars. The upper end of the pipette is passed through the lower clip and connected by caoutchouc tubing with a glass stopcock fixed in the upper clip. The other end of the stopcock is provided with a piece of

FIG. 10.

caoutchouc tubing, to which a piece of thermometer tube or a piece of wider glass tube can be attached. The wider glass tube, which serves as a mouthpiece, is first attached to the stopcock, and the pipette is filled with water to a short distance above the mark, and then emptied by the method to be adopted in its subsequent use. It is then counterpoised on the balance with the adhering water inside, the wide tube being replaced by the thermometer tube, and the requisite weights placed on the other pan. The pipette is again filled to a short distance above the mark; the thermometer tube, which is drawn out at one end, is attached again, and the stopcock is opened. Water drops very slowly from the end of the pipette, and it can be arrested the moment the balance is in equilibrium. The level of the water is marked on a piece of paper gummed to the pipette, and a new ring etched with hydrofluoric acid.
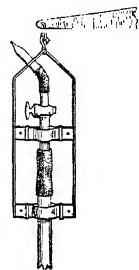
The burette is most simply calibrated by the method due to Ostwald with the help of a small pipette of about 2 c.c. capacity, attached to the burette as indicated in Fig. 11. The burette and pipette are filled with water to the zero mark and the mark a respectively, taking care to leave no air bubbles in the tubes. The clip I (or the tap of the burette) is opened and water allowed to run from the burette into the pipette till the level b is reached. The burette reading is then noted, and the pipette emptied to mark a. These operations of filling the pipette, taking

FIG. 11.

a burette reading, and then emptying the pipette, are repeated to the full extent of the burette readings. Suppose, for example, that after twenty-four fillings the burette reading is 49·49 c.c. The burette is now refilled, and exactly this amount of distilled water is run out into a tared flask and
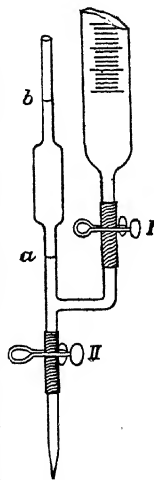
weighed, using all the precautions that would be observed in an actual titration. From the table already given the true volume of this water is calculated. Suppose this to be 49·44 c.c. Then the volume of the calibrating pipette must be $\frac{49·44}{24} = 2·060$ c.c. The differences between the successive burette readings and the successive numbers 2·06, 4·12, 6·18 . . . give at once the burette errors at these intervals, due regard being paid to the sign of the difference. In the example quoted, the correction to be applied for 50 c.c. is obviously −0·05 c.c. (*see* J. Amer. Chem. Soc. 1900, 22, 149; and for a modification of above, J. Amer. Chem. Soc. 1901, 23, 484).

A better design for a calibrating pipette is shown in Fig. 12, which also illustrates the Greiner and Friedrich three-way tap (Morse and Blalock, Amer. Chem. J. 1894, 16, 479).

The gas burettes described under *Gas analysis* may be calibrated in much the same way as an ordinary burette, by filling with water or mercury, drawing off aliquot portions and weighing them, the temperature of the liquid being noted and the appropriate correction made for expansion. Any error thus detected must be used as a correction in subsequent readings.

Standard solutions. — These form the basis of all volumetric work, and great care should be exercised in their preparation. When a solution is used only for the estimation of one substance, it may be convenient to adjust its strength so that each c.c. is equivalent to some simple and definite quantity of the substance, say 0·01 gram; but for general purposes the so-called *normal solutions* should be employed. A *normal solution* contains in 1000 c.c. the equivalent in grams of the active substance. A solution of one-tenth this strength is termed a *decinormal* solution, and one of a hundredth a *centinormal* solution. Thus a normal solution of sulphuric acid contains 49·04 grams of real acid per litre, a decinormal solution of iodine contains 12·69 grams of iodine per litre, and each litre of a decinormal solution of potassium permanganate contains 0·8 gram of active oxygen.

Standard solutions are usually made up approximately normal or decinormal as the case may be, and afterwards accurately standardised by titration against a weighed amount of some pure compound. If the solution has been purposely made rather too concentrated, it may then be suitably diluted until exactly normal or decinormal. Since accurate adjustment by dilution is difficult to effect, and in certain cases inadvisable, it is usually better to avoid the process and determine *a factor* by which readings must be multiplied in order to convert them into equivalent readings of a normal or decinormal solution. For example, if 1 c.c. of potassium permanganate solution is found to be capable of oxidising 0·005630 grams of iron, then since the corresponding figure for a decinormal solution is 0·005585, the permanganate is $\frac{5630}{5585}$, or 1·008 times decinormal, and when using it to estimate a substance of equivalent x, each c.s. of permanganate will oxidise $\frac{x}{10000} \times 1·008$ grams of substance. When only one or two litres of a standard solution are required, and the pure reagent is at hand, the exact quantity may be weighed out and diluted to the appropriate volume; e.g. solutions of silver nitrate and potassium dichromate may be thus prepared.

Measurements. — In measuring out solutions, &c., the vessels must be perfectly dry, which is inconvenient, or must be well drained and then rinsed out with a small quantity of the solution to be measured, which is allowed to run away.

To read correctly the level of the liquid in a burette or pipette requires certain precautions. In the first place, the instrument must be held in a vertical position. Ordinary liquids form a concave surface, or meniscus, and the reading should always be taken from the lowest part of this curve, except in the case of very dark-coloured solutions, when the upper line of the surface must be taken. The meniscus must be properly illuminated, and on a level with the eye, in order to avoid parallax. The best method of avoiding this error is by the use of a burette having the graduation marks carried half-way round the tube. In default of such a burette, use may be made according to Mohr of a piece of card one-half of which is black and the other half white. This is attached to the burette by an indiarubber ring, and is adjusted so that the horizontal edge of the black half, which is lowest, is 2 to 3 mm., *but not more*, below the meniscus. The lower edge of the curve then appears black against the white background. If the card is too low, the reading will be slightly too high. The little clamp and screen designed by Göckel are based on the same principle. Some burettes are provided at the back with a dark vertical line on a milk glass background. When the eye is on a level with the bottom of the meniscus, the dark line appears to be drawn out to two fine points which just touch one another. By means of these devices accurate readings can easily be taken even without using a burette float.

In addition to the errors incident to all analytical processes, another error arises in volumetric analysis, owing to variations in the concentrations of the solutions due to changes of temperature. In the case of $N/10$-solutions this affects the results to the extent of 0·1 p.c. for each 5° variation in temperature. With concentrated solutions, especially those of the acids and alkalis, the error is greater. The coefficients of expansion of certain standard solutions have been determined by A. Schulze (Zeitsch. anal. Chem. 21, 167).

Errors due to changes of temperature may be eliminated by weighing the solutions instead of measuring them. The liquid is contained in a light glass bottle, with a long jet-like neck, and a tubulus at the shoulder which can be closed by the finger, and the flow of liquid thus regulated. The bottle is weighed, the solution

FIG. 12.

poured gradually from it until the reaction is complete, and the bottle again weighed. The difference between the two weighings gives the quantity of solution used. Convenient weight burettes are described in Chem. News, 1877, 35, 98 ; J. Amer. Chem. Soc. 1908, 30, 31.

Volumetric methods may be broadly classified as I. Methods of Saturation ; II. Methods of Oxidation and Reduction ; III. Methods of Precipitation ; and examples of the two latter types of processes are indicated below. (For methods of saturation, v. ACIDIMETRY AND ALKALIMETRY.)

In the following section the methods for preparing and standardising the more commonly employed solutions are first described, followed by details of the various volumetric estimations for which these solutions may be conveniently employed, alphabetically arranged under the names of the elements that are determined.

PREPARATION OF STANDARD SOLUTIONS.

Potassium permanganate.

Employed as an oxidising agent, usually in dilute sulphuric acid solution, when the permanganate decomposes according to the equation :

$$2KMnO_4+3H_2SO_4$$
$$=K_2SO_4+2MnSO_4+3H_2O+5O.$$
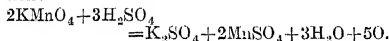
The oxidation of ferrous sulphate, for example, is represented in the following manner :—

$$2KMnO_4+10FeSO_4+8H_2SO_4$$
$$= K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O$$

and of oxalic acid thus :

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4$$
$$= K_2SO_4+2MnSO_4+8H_2O+10CO_2.$$
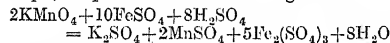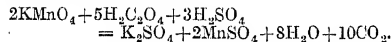
In order to facilitate calculation, these oxidations are conveniently expressed as a transference of oxygen from one oxide to another, e.g. :

$$10FeO+Mn_2O_7 = 5Fe_2O_3+2MnO.$$

The utility of permanganate solution depends upon the facts that such oxidation processes are usually quite easy to effect, the endpoint being readily indicated by the solution acquiring a faint permanent pink tinge, due to the presence of a slight excess of permanganate, which thus acts as its own indicator. Oxidation usually proceeds rapidly at the ordinary temperature, but solutions of oxalic acid must be heated to 60°–80°. It is most essential that a considerable excess of sulphuric acid should be present (about 5 c.c. of concentrated acid per 100 c.c. of solution), since otherwise the solution becomes turbid owing to the separation of manganese dioxide, and the determination is spoilt. The presence of hydrochloric acid in the solution should be avoided, if possible, since it reacts with the permanganate under certain circumstances, particularly in the presence of iron salts. The error that thus arises can be reduced to a negligible amount by adding manganese sulphate to the solution, and titrating very slowly (see Iron, p. 211).

Preparation and titration of the solution.—A decinormal solution containing 3·16 grams of the salt per litre of solution is most convenient for general use ; it is most readily prepared by grinding the solid repeatedly with small amounts

of distilled water in a mortar and decanting the solution into the stock bottle. After a day or two, the solution is filtered through asbestos, and standardised. If kept away from direct sunlight, reducing gases and dust, it retains its titre for a long time ; its spontaneous decomposition is largely augmented by the presence of solid dioxide, which explains the necessity for the filtration through asbestos (Amer. Chem. J. 1896, 18, 401).

The solution is best standardised against electrolytic iron, anhydrous sodium oxalate, or by the iodimetric method of Volhard, using a thiosulphate solution which has been recently titrated against pure iodine. (For the latter method, see *Thiosulphate solution*, and for the first, which requires a somewhat complicated apparatus, consult Treadwell-Hall, vol. 2, 81.)

Titration by sodium oxalate.—This method was proposed by Sörensen, and its accuracy has been fully established by various other chemists (Zeitsch. angew. Chem. 1902, 15, 1244 ; 1904, 17, 230 and 269 ; 1905, 18, 1520). The pure oxalate, prepared by Kahlbaum according to Sörensen's directions, should be dried at 100° for a few hours before use.

Three or four portions of the oxalate, each weighing about 0·25–0·30 grams, are dissolved in an excess of dilute sulphuric acid ; the solutions are warmed to 60°–80°, and titrated with the permanganate solution until a faint, permanent pink colouration is obtained. From the relation $2Na_2C_2O_4 = O_2$, the value of the permanganate solution is calculated for each titration, and the mean of the concordant results adopted as the true value.

Many other methods for standardising permanganate have been proposed, e.g. titration against crystalline oxalic acid $H_2C_2O_4.2H_2O$, ammonium oxalate $(NH_4)_2C_2O_4.H_2O$, ferrous sulphate $FeSO_4.7H_2O$, Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$, &c., which although at times convenient, are less accurate than the methods given. Standardisation against iron wire is not to be recommended, since the small quantities of oxidisable impurities present consume more permanganate than would be required by their own weight of iron, and the error is augmented by making allowance for the actual iron content of the wire (Zeitsch. anal. Chem. 1903, 42, 359 ; Zeitsch. angew. Chem. 1901, 14, 1233 ; also Treadwell-Hall, l.c.).

It is usual to express the concentration of a permanganate solution in terms of the amount of iron it can oxidise ; thus 1 c.c. of $N/10$-$KMnO_4 = 0·005585$ gram Fe.

Potassium dichromate.

A solution of this reagent may replace permanganate in the titration of ferrous salts, with the advantage that it can be used in the presence of either hydrochloric or sulphuric acid. An excess of free acid is essential, the oxidation of ferrous chloride, for example, proceeding according to the equation :

$$K_2Cr_2O_7+6FeCl_2+14HCl$$
$$= 2KCl+2CrCl_3+6FeCl_3+7H_2O$$
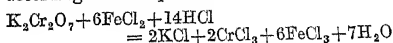
which is essentially :

$$2CrO_3+6FeO = Cr_2O_3+3Fe_2O_3.$$
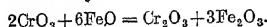
A decinormal solution obtained by dissolving

$\dfrac{K_2Cr_2O_7}{60} = 4.903$ grams of the pure dry re-crystallised salt in distilled water and diluting the solution to 1 litre, requires no further standardisation. A stock solution of approximate strength may be standardised against several weighed amounts (1·0–1·4 grams) of pure ferrous ammonium sulphate by a similar procedure to that described under the standardisation of permanganate by sodium oxalate. The titrations, however, are made in cold solution, and the dilute sulphuric acid used should be gently boiled for half an hour to expel dissolved air, and cooled rapidly just before use. Since the green colour of the chromic salt prevents the excess of dichromate from being seen, an external indicator is necessary. Drops of a *dilute* solution of potassium ferricyanide, free from ferrocyanide, are placed on a white plate, and from time to time the end of a glass rod, previously dipped in the titrating flask, is brought into contact with a drop of the ferricyanide. As long as any ferrous salt remains a blue precipitate is produced; the approach of the end is indicated by the decrease in intensity of the blue colouration, and when very near the end about thirty seconds should be allowed for the colour to develop. The end-point is reached when the blue colour ceases to appear. The ferricyanide solution should be prepared only when required by dissolving in water a crystal of the salt which has been rinsed to remove superficial ferrocyanide : the yellow colour of the drops on the white plate should be barely visible ; if the ferricyanide is too concentrated, the blue colouration changes through various shades of green into a brown tint.

Iodine, Sodium thiosulphate, and Sodium arsenite.

Decinormal solutions of these reagents are frequently used in conjunction with one another. The reaction between iodine and sodium thiosulphate is essentially :

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$
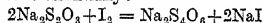
although under certain circumstances oxidation to sulphate proceeds to a small extent, even at the ordinary temperature (Pickering). When using decinormal solutions the end-point is readily indicated by the appearance or disappearance of the yellow colour of the iodine, provided the solution undergoing titration is not unduly diluted and is otherwise colourless. The production of a blue colour when free iodine and starch solution are brought together is, however, much more sensitive, and is the method usually employed in ascertaining the end-point.

Preparation of starch solution.—About 1 gram of powdered starch is rubbed into a paste with a little cold water, and slowly added to 200 c.c. of boiling water, the boiling is continued for two or three minutes, the solution cooled, and after some hours the clear liquid is decanted. The solution will only keep for one or two days, unless sterilised, when it is conveniently preserved in small bottles, completely filled and closed by soft rubber stoppers ; it will then keep indefinitely. Starch paste prepared from Gastine's formula (5 grams starch, 0·01 gram mercuric iodide, and 1 litre water) retains its sensitiveness for a long time. Addition of 1 c.c.

of oil of cassia to a litre of starch liquor is also recommended as a preservative.

Sensitiveness of the iodine-starch reaction.—This depends upon several circumstances. It is necessary to work with cold solutions, preferably neutral or slightly acid ; the presence of mineral acid in high concentration greatly impairs the sensitiveness of the reaction, since it hydrolyses the starch. It is essential that a soluble iodide should be present (usually this is potassium iodide) in moderate amount ; the best concentration of potassium iodide to employ is about $N/150$, since the sensitiveness of the reaction then reaches a maximum (see Zeitsch. anal. Chem. 1902, 41, 485 ; Amer. J. Sci. 1900, [iv.] 10, 151 ; J. Amer. Chem. Soc. 1909, 31, 1038).

Good starch solution first yields a pink colouration with iodine, which more iodine develops into the blue colour ; starch which produces green tints should be rejected (J. Amer. Chem. Soc. 1908, 30, 31). It frequently happens in titrating arsenious and antimonious oxides with iodine that various tints of red make their appearance instead of the usual blue colouration. This is due to impurity in the starch : in such a case one or two grams of potassium iodide are added, the end-point being ascertained from the development of the yellow colour of the iodine, and then confirmed by the starch (Amer. J. Sci. 1902, [4] 13, 379).

For the *iodine solution* 25 grams of potassium iodide are dissolved in a little water, 12·7 grams of commercial iodine added, and the mixture shaken till the iodine has dissolved ; the solution is then filtered through asbestos and diluted to 1 litre. It should be kept in the dark, and protected from dust. For the *thiosulphate solution* the crystalline salt $Na_2S_2O_3$, $5H_2O$ is dissolved in distilled water, using 25 grams per litre, and the solution kept away from direct sunlight for two weeks before it is standardised. It then retains its titre for months. For the *sodium arsenite*, 4·948 grams of resublimed arsenious oxide are dissolved in a little warm sodium hydroxide free from iron, the solution rinsed into a litre flask, and made just acid to phenolphthaleïn with dilute sulphuric acid. A filtered solution of 20 grams of sodium bicarbonate in 500 c.c. of water is added, and if the mixture reacts alkaline to the phenolphthaleïn, sulphuric acid added till the pink colour disappears. This solution, when diluted to 1 litre and thoroughly mixed, is strictly decinormal, and keeps indefinitely. A measured quantity of the $N/10$-arsenite solution is delivered into an Erlenmeyer flask, and the iodine solution run in from the burette until present in slight excess, starch paste being added nearly at the finish of the titration (see remarks on starch above). The reaction

$$As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI$$
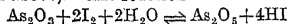
proceeds to completion in the sense of the upper arrow in neutral solution, a condition secured by the presence of the bicarbonate, which neutralises the hydriodic acid produced. Since the solution should be saturated with carbon dioxide, it is advisable to stopper the flask except when actually introducing the iodine (J. Amer. Chem. Soc. 1908, 30, 31).

The iodine being standardised, the thio-

sulphate can be directly titrated against it, preferably by running the iodine into a measured volume of thiosulphate.

Many alternative methods have been proposed for standardising iodine and thiosulphate solutions. The latter may be titrated against pure iodine : 0·5 gram of pure iodine and 0·1 gram of potassium iodide are powdered and mixed together in a porcelain dish, and heated on a sand-bath till vapour is copiously evolved ; the dish is then covered with a dry watch-glass, and the greater part of the iodine sublimed on to it. The watch-glass is covered with a second accurately fitting glass and the whole weighed, the weight of the glasses having been previously found. The whole is gently placed in a solution of 1 gram of potassium iodide in 10 c.c. of water, and after a few seconds the solution is diluted to 100 c.c. and titrated with the thiosulphate.

The thiosulphate may also be standardised against permanganate, itself verified by reference to sodium oxalate. One or two grams of potassium iodide are dissolved in water, acidified with 5 c.c. of hydrochloric acid (1 : 5) and 25 c.c. of standard permanganate added. The iodine, which is quantitatively liberated :

$$Mn_2O_7 + 10HI = 2MnO + 5H_2O + 5I_2$$
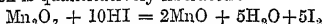
is then titrated with the thiosulphate, after diluting the solution to 100 c.c. By the reverse process of calculation, a permanganate solution may be standardised against a thiosulphate solution that has been verified by either of the preceding methods (*see Standardisation of permanganate; cf.* Annalen, 1897, 198, 333 ; Zeitsch. angew. Chem. 1904, 17, 815 ; Ann. Chim. Anal. 1904, 9, 365 ; Zeitsch. anorg. Chem. 1906, 49, 277).

(For the use of potassium dichromate in this connection, *see Volumetric estimation of chromium;* Zeitsch. anorg. Chem. 1899, 19, 427 ; 1906, 49, 277. *See* also *Copper* under *Volumetric estimations.* For a gravimetric method for standardising iodine solution, consult Amer. J. Sci. 1909, (iv.) 28, 33.)

Titanous chloride.

This reagent, introduced into volumetric analysis by Knecht (J. Soc. Dyers and Colourists, 19, No. 6; Ber. 1907, 40, 3819), is a powerful reducing agent. For example, a hydrochloric acid solution of ferric chloride is quickly and quantitatively reduced in the cold, according to the equation :

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$$
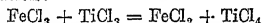
and the end-point is reached when a drop of the liquid ceases to produce a red colouration with potassium thiocyanate. Chromic acid and cupric salts may be similarly estimated, and also a large number of organic dyes.

Fifty c.c. of the commercial 20 p.c. solution of titanous chloride, which usually contains a little iron, are mixed with an equal volume of concentrated hydrochloric acid, boiled for several minutes, and diluted to 1 litre with air-free water. The solution must be kept protected from the air : a convenient method is figured in Sutton's Volumetric Analysis (9th ed.), p. 224.

The concentration of the solution is fixed by titrating against a known quantity of either ferric salt or potassium dichromate. In the

former case 35 grams of pure ferrous ammonium sulphate are dissolved in dilute sulphuric acid and the solution diluted to 1 litre ; 25 c.c. are then exactly oxidised with dilute permanganate, and the resulting ferric sulphate titrated with the titanous chloride until a drop of the solution no longer gives a red colour with potassium thiocyanate. Instead of using this 'spot-out' method, 10–20 c.c. of 10 p.c. potassium thiocyanate may be added to the ferric solution. If the standardisation be effected with potassium dichromate, addition of the indicator to the solution itself is inadmissible. Nearly all the titanous chloride necessary, may, however, be added at once, since the colour changes, through orange to green and then violet, afford an indication of the end-point. Drops of solution are removed for testing when the green colour has just disappeared (J. Soc. Chem. Ind. 1908, 27, 673).

Pure ferric alum, the preparation of which is described by De Koninck (Bull. Soc. chim. Belg. 1909, 23, 222), might also be employed for this standardisation.

For a number of estimations it is necessary to employ titanous sulphate instead of the chloride.

Stannous chloride.

This reagent has long been employed as a reducing agent, but the closely allied and more powerfully reducing titanous salts appear to be displacing it. Ferric salts are easily reduced in hot acid solution :

$$2FeCl_3 + SnCl_2 = SnCl_4 + 2FeCl_2.$$
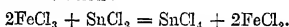
Iodine in cold acid solution oxidises it quantitatively :

$$2SnCl_2 + 2I_2 = SnI_4 + SnCl_4.$$

Ten grams of pure tin in thin pieces are heated with 200 c.c. of concentrated hydrochloric acid in a platinum dish until dissolved : or a glass flask may be used with a piece of platinum foil touching the tin to promote its speedy solution. The solution is diluted to 1 litre, and preserved out of contact with the air.

The solution is best standardised by that process for which it is afterwards to be employed, *e.g.* if required for iron estimations, by titration against a known amount of ferric chloride. The latter may be obtained by dissolving 10·03 grams of bright iron wire (99·7 p.c. iron) in hydrochloric acid, oxidising with potassium chlorate, expelling the excess of chlorine by boiling, and diluting the solution to 1 litre ; 25 c.c. are conveniently used for titrating the above solution.

Several methods have been proposed for determining the end-point. The iron solution containing 20–40 c.c. of concentrated hydrochloric acid in a volume of 125 c.c. may be titrated nearly at the boiling-point, 15 c.c. of indicator solution (34 grams $HgCl_2 + 0·05$ gram Pt as chloride per litre) being added. The end-point is reached when a dark-cloud of finely divided mercury and platinum is produced (Amer. Chem. J. 1893, 15, 360). Or a drop of the solution may be mixed with ammonium molybdate on a white plate ; the slightest trace of stannous salt causes a blue colouration. An alternative is to add a slight

excess of stannous chloride, and titrate back the cold solution with iodine.

(For the standardisation by means of iodine, see *Volumetric estimation of tin*.)

Silver nitrate, Sodium chloride, and Ammonium thiocyanate.

These precipitation reagents, which are conveniently made of decinormal strength, are of great service for the volumetric estimation of silver, copper, mercury, the halogen acids, cyanides, and thiocyanates.

Silver nitrate is used either in neutral or in nitric acid solution. In the first case potassium chromate is employed as indicator when halogens are being estimated (Mohr's method). Silver chromate is decomposed by solutions of halogen salts forming silver halide and metallic chromate; consequently, silver chromate cannot permanently exist in the solution until all the halogen has been precipitated. The first drop of silver nitrate in excess then produces a permanent precipitate of silver chromate, which gives a faint red tint to the previously pale-yellow liquid. This colour change is more readily observed in monochromatic light (from a powerful sodium flame). One or two drops of a 10 p.c. solution of potassium chromate are added to the solution, which should not be unduly diluted. Silver chromate is soluble in mineral acids or ammonia; hence the necessity for working in neutral solution. An alkaline solution may be acidified with dilute nitric acid, and then neutralised with powdered calcium carbonate. Barium must be absent from the solution, since it precipitates the indicator; it may be removed with sodium sulphate.

In the presence of nitric acid, silver nitrate and ammonium thiocyanate solutions are used in conjunction (Volhard's method, Annalen, 1878, 190, 47). The addition of thiocyanate to a nitric acid solution containing silver causes the precipitation of white silver thiocyanate, and the end-point is indicated by the red colouration produced by the interaction of the first drop of thiocyanate in excess with a ferric salt previously introduced into the solution. The thiocyanate should always be added to the silver solution. The ferric indicator is prepared by adding nitric acid (4:1 boiled to expel nitrous acid) to a saturated solution of iron alum until colourless; 5–10 c.c. are used in the titration.

Standard sodium chloride solution is used for the estimation of silver by the very exact method originally due to Gay-Lussac. (For a description of the method, *v.* ASSAYING.)

Decinormal silver nitrate is obtained by dissolving 16·99 grams of the pure dry recrystallised silver nitrate in water and diluting the solution to 1 litre. If it is to be used in conjunction with the thiocyanate, this solution may also be prepared by dissolving 10·788 grams of pure silver in a slight excess of nitric acid, boiling till nitrous acid is expelled, and diluting to 1 litre.

The thiocyanate is prepared approximately decinormal by dissolving the salt in distilled water (8 grams per litre), and is standardised against the silver nitrate solution, 25 c.c. of which are diluted to 100 c.c. and titrated as described above.

VOLUMETRIC ESTIMATIONS.

Aluminium. *Iodimetrically.* The neutral solution is boiled with excess of potassium iodide and potassium iodate for twenty minutes in a stream of hydrogen; the iodine evolved, and collected in potassium iodide, together with that which remains in the distilling flask, is titrated with $N/10$-thiosulphate (Amer. J. Sci. 1905, 20, 181; Zeitsch. anorg. Chem. 1907, 52, 286):

$$Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2.$$
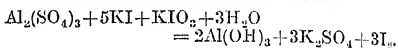
Antimony. ANTIMONIOUS SOLUTIONS. (*a*) *Iodimetrically.* One or two grams of Rochelle salt are added, the solution made alkaline with sodium bicarbonate, and titrated with $N/10$-iodine. $I_2 = Sb$ (*v.* ARSENIC).

(*b*) *By oxidation.* The hot hydrochloric acid solution (above 60°) is titrated with $N/10$-potassium bromate, which has been standardised against a known amount of pure antimony—

$$3SbCl_3 + KBrO_3 + 6HCl = 3SbCl_5 + KBr + 3H_2O.$$
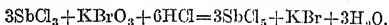
The end-point is indicated by the bleaching of a few drops of methyl orange added to the hot solution (Chem. Zeit. 1903, 27, 749; J. Soc. Chem. Ind. 1906, 25, 1181; Chem. News, 1907, 95, 49).

(*c*) *By oxidation.* The cold solution, freely acidified with hydrochloric acid, is titrated with $N/10$-permanganate (Zeitsch. angew. Chem. 1901, 14, 1179; J. Amer. Chem. Soc. 1907, 29, 66).

ANTIMONIC SOLUTIONS. (*a*) *By reduction* to the tervalent state, and estimation by one of the foregoing processes. Reduction may be accomplished: (i.) by boiling the hydrochloric acid solution with sodium sulphite or sulphurous acid (Zeitsch. angew. Chem. 1888, 155); according to Rohmer, the reduction is not quantitative unless a gram of potassium bromide is added (Ber. 1901, 34, 1565); (ii.) by boiling the sulphuric acid solution (100 c.c. containing 5 c.c. of concentrated acid and 4 grams of Rochelle salt) with 1·0–1·5 grams of potassium iodide till nearly all the iodine is expelled, exactly bleaching the remainder with dilute sulphurous acid, diluting, rapidly cooling, and neutralising. The solution is then titrated in bicarbonate solution with $N/10$-iodine (Amer. J. Sci. 1892, 42, 213).

(*b*) *Iodimetrically.* The cold solution containing 20–25 c.c. of hydrochloric acid in a volume of 100 c.c., is mixed with 0·5–1·0 gram of potassium iodide and the liberated iodine titrated with $N/10$-thiosulphate. $I_2 = Sb$ (Zeitsch. anorg. Chem. 1908, 58, 202; cf. *ibid.* 1903, 37, 337).

Arsenic. ARSENIOUS SOLUTIONS. *Iodimetrically.* The solution, containing sodium bicarbonate in excess, is titrated with $N/10$-iodine as described under the standardisation of iodine solution. The bicarbonate may with advantage be replaced by disodium hydrogen phosphate (J. Amer. Chem. Soc. 1908, 30, 31).

ARSENIC SOLUTIONS. (*a*) *By reduction* with hydriodic acid as described under *Antimony*, and subsequent titration with iodine; no Rochelle salt is necessary (Amer. J. Sci. 1900, 10, 151). Reduction may also be effected by heating the sulphuric acid solution with sulphurous acid in a stoppered bottle for an hour, diluting and boiling down to half the volume to expel excess

of sulphurous acid (Zeitsch. anal. Chem. 1883, 22, 378 ; Chem. News, 1886, 53, 221).

(b) *By precipitation.* The neutral or acetic acid solution is precipitated with excess of silver nitrate, and the precipitated silver arsenate collected, washed, dissolved in nitric acid, and the silver titrated with $N/10$-thiocyanate. $3Ag=As$.

(c) *Iodimetrically* (Zeitsch. anal. Chem. 1906, 45, 596 ; compare Amer. J. Sci. 1900, 10, 151). (*See* also Zeitsch. anorg. Chem. 1909, 62, 123, for a method suitable for small quantities of arsenic.)

Barium. *Iodimetrically.* Excess of potassium iodate is added to the faintly ammoniacal solution, the precipitated iodate washed with ammonia and then with alcohol, dissolved in hydrochloric acid and potassium iodide, and the iodine titrated with $N/10$-thiosulphate. $6I_2=Ba$ (J. Amer. Chem. Soc. 1909, 31, 43).

Bismuth. (a) *Iodimetrically.* The solution, as free as possible from mineral acids, is mixed with excess of $N/2$-potassium chromate, shaken for 10 minutes, diluted to a known volume, and the chromate in an aliquot part of the filtrate from the bismuthyl chromate $Bi_2O_3 \cdot 2CrO_3$ is titrated iodimetrically (Zeitsch. anorg. Chem. 1902, 32, 362 ; Zeitsch. anal. Chem. 1907, 46, 223).

(b) As *bismuth ammonium molybdate* (J. Amer. Chem. Soc. 1903, 25, 907).

Boron. (a) *v.* ACIDIMETRY AND ALKALIMETRY.

(b) *Iodimetrically.* The reaction

$$5KI+KIO_3+6HBO_2=3I_2+3H_2O+6KBO_2$$
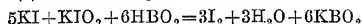
is quantitative in a solution saturated with mannitol (*v.* Amer. J. Sci. 1899, 8, 127).

Bromine *v. Halogens.*

Calcium. *By oxidation.* The oxalate, precipitated from a hot slightly ammoniacal solution (*see Gravimetric methods*), is washed with warm water till free from ammonium oxalate, decomposed with hot dilute sulphuric acid, and the oxalic acid titrated with $N/10$-permanganate. The precipitate may also be dissolved in dilute hydrochloric acid, 0·5 gram of manganese sulphate added, and the solution titrated with permanganate (*v.* Amer. Chem. J. 1905, 33, 500).

Carbon. CARBON DIOXIDE. *v.* ACIDIMETRY and ALKALIMETRY, and *Gas analysis.*

CYANOGEN ACIDS. CYANATES. The cold, dilute solution is exactly neutralised with $N/10$-hydrochloric acid (using methyl orange or congo red as indicator), excess of acid is added, the solution boiled for ten minutes, cooled and titrated back $N/10$-sodium hydroxide. Excess of $N/10$-sodium hydroxide is then added, the solution boiled to expel ammonia, and titrated back with $N/10$-hydrochloric acid. From these data two values for the cyanate can be calculated, which serve to check one another (Chem. News, 1906, 93, 5 ; compare Zeitsch. angew. Chem. 1901, 24, 585 ; J. Soc. Chem. Ind. 1904, 23, 244).

$$KCNO+2HCl+H_2O = KCl+NH_4Cl+CO_2.$$
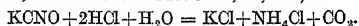
CYANIDES. (a) *By precipitation.* (i.) Excess of $N/10$-silver nitrate is added to the neutral cyanide solution, and then a little nitric acid. The excess of silver is titrated with $N/10$-thiocyanate after filtering off the silver cyanide. (ii.) The slightly alkaline solution is titrated with $N/10$-silver nitrate with constant stirring

till a permanent turbidity is produced (Liebig, Annalen, 1851, 77, 102). This marks the end of the reaction :

$$2KCN+AgNO_3=KNO_3+KAg(CN)_2.$$
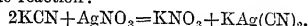
The end-point is best observed by adding 5–10 drops of 20 p.c. potassium iodide as an indicator. A permanent yellow turbidity, due to silver iodide, is produced as soon as the above reaction is completed (Ann. Chim. Phys. 1895, (vii.) 6, 381).

(b) See *Ferrocyanides* (b).

FERRICYANIDES. (a) The salt is reduced to ferrocyanide by boiling with sodium hydroxide and ferrous sulphate and the filtered solution strongly acidified with sulphuric acid and titrated with $N/10$-permanganate (*v. Ferrocyanides.* Reduction may also be effected by boiling with sodium peroxide (Arch. Pharm. 232, 226).

(b) *Iodimetrically.* The neutral solution (50 c.c.) is mixed with 3 grams of potassium iodide and 1·5 grams of zinc sulphate, the mixture well shaken, and the iodine titrated with $N/10$-thiosulphate. $2K_3Fe(CN)_6=I_2$ (Zeitsch. anorg. Chem. 1910, 67, 418 ; compare *ibid.* 67, 322).

FERROCYANIDES. (a) *By oxidation.* The solution is strongly acidified with sulphuric acid and titrated with $N/10$-permanganate till the colour changes from yellowish-green to yellowish-red. If any difficulty is experienced in determining the end-point, a drop of the solution may be mixed with dilute ferric chloride. A blue colour will develop whilst any ferrocyanide remains (de Haen, Annalen, 1854, 90, 160 ; compare Zeitsch. anorg. Chem. 1910, 67, 418).

An excess of permanganate may also be added, the excess being determined iodimetrically. (For details, consult Zeitsch. anorg. Chem. 1910, 67, 322.)

(b) *By conversion into hydrocyanic acid.* The ferrocyanide solution is boiled for five minutes with 10 c.c. of N-sodium hydroxide and 15 c.c. of $3N$-magnesium chloride, 100 c.c. of boiling $N/10$-mercuric chloride are then added, and the boiling continued for ten minutes. The mercuric cyanide produced is distilled for thirty minutes with 30 c.c. of $3N$-sulphuric acid, the prussic acid collected in 25 c.c. of N-sodium hydroxide, a little potassium iodide added, and the cyanide titrated with $N/10$-silver nitrate (Feld, Chem. Zentr. 1903, ii. 1398 ; Analyst, 1908, 33, 261 ; 1910, 35, 295).

THIOCYANATES. (a) *By precipitation.* As in standardising ammonium thiocyanate solution ; the thiocyanate must be added to the silver nitrate, and not *vice versâ*, since nitric acid decomposes thiocyanates.

(b) *By oxidation.* The thiocyanate is titrated in concentrated hydrochloric acid solution with potassium iodate, in a stoppered bottle, with vigorous shaking. The end-point is reached when 5 c.c. of chloroform previously introduced are no longer coloured by iodine (J. Amer. Chem. Soc. 1908, 30, 760) ; *e.g.*

$$4CuCNS+7KIO_3+14HCl$$
$$=4CuSO_4+7KCl+7ICl+4HCl+5H_2O.$$
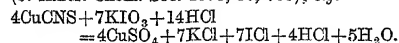
Oxidation in dilute sulphuric acid solution with permanganate is untrustworthy.

Cerium. (a) *Iodimetrically.* Ceric oxide is warmed with concentrated hydrochloric acid and potassium iodide in a stoppered bottle till complete solution is effected. The liberated

iodine is then titrated with $N/10$-thiosulphate (Bunsen, Annalen, 1858, 105, 49; also Amer. J. Sci. 1899, 8, 451).

$$2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 2KCl + I_2 + 4H_2O$$
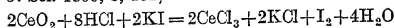
(b) *By oxidation.* The washed oxalate is suspended in hot dilute sulphuric acid and titrated with $N/10$-permanganate (v. *Calcium:* Zeitsch. anal. Chem. 1880, 19, 194; Amer. J. Sci. 1899, 8, 457).

(c) *By reduction.* The cerium is oxidised with sodium bismuthate in boiling sulphuric acid solution to ceric sulphate and the filtered solution reduced by a slight excess of ferrous sulphate, the excess being titrated with $N/10$-permanganate. Other rare earth metals do not interfere (J. Amer. Chem. Soc. 1909, 31, 523; 1910, 32, 642; compare Compt. rend. 1899, 128, 101; Ber. 1900, 33, 1924; Ber. 1903, 36, 282).

(d) *Other methods* (Zeitsch. anorg. Chem. 1907, 54, 104; 1908, 59, 71).

Chlorine v. *Halogens.*

Chromium. The chromium should be in the form of chromate.

(a) *Iodimetrically.* The chromate solution is acidified with hydrochloric acid (5 c.c. of concentrated acid per 100 c.c. solution), 1 or 2 grams of potassium iodide added, and the covered solution allowed to stand for 15 to 20 minutes. It is then diluted to 400–500 c.c. and the liberated iodine titrated with $N/10$-thiosulphate. $3I_2 = 2Cr$. A known dichromate solution can in this way be used to standardise sodium thiosulphate (J. pr. Chem. 1868, 103, 362; Zeitsch. anorg. Chem. 1899, 19, 427; 1906, 49, 277; Zeitsch. angew. Chem. 1900, 1147).

(b) *By reduction* (i.) with ferrous ammonium sulphate, of which a slight excess is added to the chromate solution containing sulphuric and hydrochloric acid, the excess of ferrous salt being then titrated with $N/10$-dichromate; (ii.) with titanous chloride (v. *Preparation of standard solutions;* J. Soc. Chem. Ind. 1908, 27, 673); (iii.) with arsenious oxide (Amer. J. Sci. 1896, 1, 35).

Chromium in chrome steel. Three grams of alloy are dissolved in 35 c.c. of concentrated hydrochloric acid, and the excess evaporated; 150 c.c. of strong nitric acid are added, the boiling continued till no more brown fumes are evolved, when all chlorine has been expelled. The chromium is then oxidised by adding 10 grams of potassium chlorate, and the solution boiled down to 40 c.c. to decompose excess of chlorate; 100 c.c. of water are added, and one or two drops of hydrochloric acid, to dissolve separated manganese dioxide. The chromate solution is boiled to expel chlorine, cooled and titrated according to method (b) (i.) above. (For other methods, *see* J. Amer. Chem. Soc. 1905, 27, 1550; 1908, 30, 1116; J. Soc. Chem. Ind. 1907, 26, 1010; Chem. News, 1904, 90, 320; 91, 3; also *Manganese* and *Vanadium* (v. *infra*).)

Chromium in chromite. The valuation of this, the only important ore of chromium, is usually effected by a volumetric method; the finely powdered ore is fused with sodium peroxide in a nickel crucible, and the chromate in the aqueous extract estimated as described above, after boiling for ten minutes to decompose

excess of peroxide (v. J. Soc. Chem. Ind. 1896, 15, 155, 436; Chem. Zeit. 1897, 21, 3; Bull. Soc. Chim. 1909, 5, 1133; Chem. News, 1896, 73, 1).

Cobalt. (a) *Iodimetrically.* The solution is mixed with hydrogen peroxide, and then with sodium hydroxide, when the cobalt is precipitated as sesquioxide Co_2O_3, whilst nickel is simply precipitated as green hydroxide. After boiling for a minute, the black ppt. is dissolved in hydrochloric acid and potassium iodide, and the iodine titrated with $N/10$-thiosulphate (Chem. News, 1900, 82, 66, 73; 1903, 88, 184).

(b) *By precipitation* with ferrocyanide, as described under *Nickel* (b).

Columbium. *By reduction and subsequent oxidation* (v. Zeitsch. anorg. Chem. 1909, 62, 383).

Copper. (a) *Iodimetrically.* The solution of cupric salt preferably neutral or containing acetic acid, is diluted to 100 c.c., 5 grams of potassium iodide are added, and the liberated iodine titrated with $N/10$-thiosulphate, using starch paste as indicator. If more than 25 c.c. of thiosulphate are required, 2–3 grams more potassium iodide should be added (Amer. J. Sci. 1907, 24, 65; compare J. Amer. Chem. Soc. 1902, 24, 1082; 1905, 27, 1224; see also *Methods of separation*).

$$2CuSO_4 + 4KI = 2K_2SO_4 + I_2 + Cu_2I_2.$$
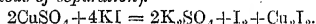
(b) *By titration with potassium cyanide* (*Steinbeck's process*). The ammoniacal copper solution is titrated with potassium cyanide until colourless (v. Chem. News, 1897, 76, 189; *Methods of separation;* and the article COPPER).

(c) *By precipitation as thiocyanate* and estimation of the precipitate by potassium iodate in hydrochloric acid solution (v. *Thiocyanates;* and J. Amer. Chem. Soc. 1908, 30, 700).

(d) *By oxidation.* The oxalate is precipitated in a nitric acid solution by adding excess of ammonium oxalate, washed and titrated with $N/10$-permanganate (Amer. J. Sci. 1909, 27, 448).

(e) *By reduction* to cuprous salt. To the sulphuric or hydrochloric acid solution, 10–20 c.c. of 10 p.c. potassium thiocyanate and a little ferrous salt are added, when a deep red colouration is produced, since ferrous salts in acid solution are partly oxidised by cupric salts. The cold solution is titrated with titanous chloride until the red colouration is destroyed (Chem. Soc. Trans. 1906, 89, 1491). Or a slight excess of titanous chloride may be added, and titrated back with standard ferric alum.

Fluorine. *Acidimetrically.* The fluoride is mixed with ten times its weight of finely powdered and ignited quartz, and decomposed by warming with concentrated sulphuric acid; the silicon fluoride evolved passes through a dry U-tube filled with glass beads and immersed in cold water, in order to remove sulphuric acid, and is then absorbed in 50 p.c. alcoholic potassium chloride, which precipitates silicic acid and potassium silicofluoride, leaving hydrochloric acid in the solution :—

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$$
$$H_2SiF_6 + 2KCl = K_2SiF_6 + 2HCl.$$
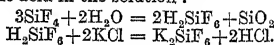
The hydrochloric acid is titrated with $N/5$-sodium hydroxide, using lacmoid as indicator. $2HCl = 3F_2$. (For full experimental details, which are absolutely essential in order to obtain

accurate results, consult Chem. News, 1879, 39, 179; Amer. J. Sci. 1906, 22, 329; or Low's Technical Methods of Ore Analysis.)

Gold. *Iodimetrically.* The auric solution is treated with potassium iodide in more than sufficient quantity to dissolve the aurous iodide first precipitated, and the iodine liberated is estimated with standard thiosulphate (Amer. J. Sci. 1899, 8, 261; compare Zeitsch. anorg. Chem. 1899, 19, 63).

Halogens. This term is restricted in this connection to chlorine, bromine, and iodine, fluorine being treated separately, since its analytical reactions are quite different.

ESTIMATION OF HALOGENS. *Iodine* is estimated by solution in potassium iodide and titration with $N/10$-thiosulphate, using starch paste as indicator (*v. Preparation of standard solutions*, p. 205). *Bromine* and *chlorine* are absorbed in potassium iodide solution, setting free an equivalent quantity of iodine, which is titrated with $N/10$-thiosulphate.

A large number of substances, *e.g.* peroxides, chlorates, chromates, &c., may be readily determined indirectly by distillation with concentrated hydrochloric acid, the available oxygen of the compound setting free its equivalent of chlorine, which is absorbed in potassium iodide, and the liberated iodine titrated with $N/10$-thiosulphate. It is very desirable to exclude air in the process of distillation, since it liberates iodine from the hydrogen iodide set free in the receiver, by the hydrogen chloride distilling over during the experiment. The apparatus devised by Bunsen, the originator of this analytical method, is shown in Fig. 13, *b*. The
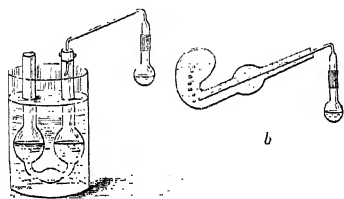
FIG. 13.

small flask (50 c.c.) and the delivery tube are ground at their junction to fit, and the joint made with caoutchouc tubing; a ground-glass joint is better, a spring holding the two parts tightly together. The mixture is rapidly boiled, the chlorine passing into potassium iodide contained in the retort, the size of which must be suitably chosen to prevent overflowing. A different receiving vessel is shown in Fig. 13, *a*. It is very convenient to perform such distillations in a current of carbon dioxide or other inert gas, and various designs of apparatus for such a purpose are given in Amer. J. Sci. 1898, 6, 168; Chem. News, 1899, 79, 85; Chem. Soc. Trans. 1892, 61, 87; Zeitsch. angew. Chem. 1890, 477.

The apparatus shown in Fig. 14 (Analyst, 1908, 33, 117) admits of the gradual introduction of a liquid reagent during distillation in carbon dioxide, steam, or any other gas or vapour. Contamination of the reagents with cork or

VOL. I.—*T*.

indiarubber derived from stoppers, &c., is avoided by fitting the condenser and the dropping
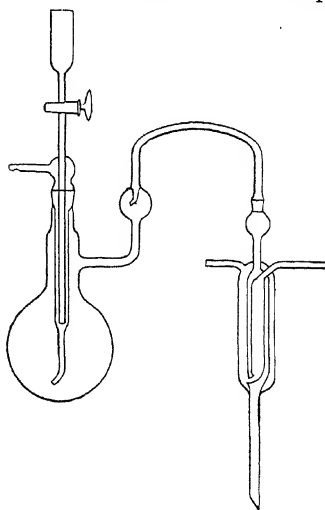
FIG. 14.

funnel to the distilling flask by ground-glass joints.

ESTIMATION OF HALOGENS IN HALIDE SALTS. *By precipitation.* (i.) *Mohr's method.* The neutral solution is titrated with $N/10$-silver nitrate in the presence of a few drops of potassium chromate as indicator (*v. Preparation of standard solutions*, p. 206). It is advisable to perform a blank experiment under identical conditions, to allow for the silver nitrate necessary to bring out the reddish colouration. (ii.) *Volhard's method.* The nitric acid solution of the halide is precipitated by adding a slight excess of $N/10$-silver nitrate, the excess being then titrated with $N/10$-ammonium thiocyanate. Silver chloride must be filtered off before the latter titration is performed, since it reacts with the thiocyanate (J. Amer. Chem. Soc. 1907, 29, 269; compare Zeitsch. anorg. Chem. 1909, 63, 330); but silver bromide and iodide do not interfere. It is advisable to titrate iodide in a stoppered bottle with vigorous shaking when adding both the silver solution and the thiocyanate, to minimise error due to occlusion. It is more accurate to weigh out a very slight excess of pure silver, dissolve it in nitric acid (carefully expelling nitrous acid, which interferes with the indicator), and add to the halide solution than to measure out $N/10$-silver nitrate. After vigorous shaking, the excess of silver is then titrated with a dilute thiocyanate solution (1 c.c. = 1 milligram Ag).

IODIDES. *Iodimetrically.* (i.) A slight excess of potassium iodate is added, and the solution acidified with dilute sulphuric acid. The liberated iodine is extracted with chloroform, carbon disulphide or toluene, and titrated with $N/10$-thiosulphate. A weaker acid than sulphuric acid may be employed, *e.g.* acetic or

tartaric acid. Five-sixths of the iodine found was originally present as iodide (Chem. Zeit. 1904, 28, 1191 ; Amer. J. Sci. 1897, 3, 293 ; J. pharm. Chim. 1902, 16, 207 ; J. Amer. Chem. Soc. 1903, 25, 1138). This method is available in the presence of bromide and chloride, if acetic acid be employed. (ii.) The solution, containing the iodide, 2 grams of pure potassium arsenate, and 10 c.c. of concentrated sulphuric acid, is boiled down from a volume of 100 c.c. to 35–40 c.c., when all the iodine is expelled. The arsenious salt in solution is then titrated with $N/10$-iodine (Amer. J. Sci. 1890, 39, 188). As $=I_2$. In the presence of chloride the results are a little low; bromide causes them to be slightly high. (iii.) (v. Chem. Soc. Trans. 1885, 47, 471.)

ESTIMATIONS OF HALOGENS IN OXYHALOGEN COMPOUNDS. (a) By reduction to a halide salt and determination of the latter. Iodates are reduced by adding sulphurous acid to the sulphuric acid solution of the iodate till the separated iodine is redissolved ; an excess of $N/10$-silver nitrate is added to precipitate the iodide, the mixture boiled with excess of nitric acid, and finally the excess of silver titrated with $N/10$-thiocyanate. Bromates and chlorates are reduced by adding an excess of iron filings to the sulphuric acid solution ; after an hour, excess of $N/10$-silver nitrate is added, the mixture boiled with nitric acid to oxidise the ferrous salt, and the excess of silver titrated (Amer. Chem. J. 1904, 32, 242).

(b) By reduction to a halide salt and estimation of the reducing agent used up in the process. With chlorates and bromates, the sulphuric acid solution is boiled for ten minutes with excess of standard ferrous sulphate in an atmosphere of carbon dioxide, the solution cooled, manganese sulphate added and the unchanged ferrous salt titrated with $N/10$-KMnO$_4$. $6Fe = ClO_3$ or BrO_3 (Zeitsch. anorg. Chem. 1904, 38, 110). Bromates may also be reduced with arsenious oxide (Amer. J. Sci. 1902, 14, 285). Chlorates are reduced by adding an excess of $N/10$-titanous sulphate, and after three minutes, titrating back with ferric alum (J. Soc. Chem. Ind. 1908, 27, 434).

(c) Iodimetrically. Chlorates. (i.) By distillation with concentrated hydrochloric acid. $ClO_3 = 3I_2$ (Bunsen's method ; v. Estimation of halogens ; Chem. Soc. Trans. 1892, 61, 87). (ii.) By reduction with concentrated hydrochloric acid and potassium bromide (Chem. Zeit. 1901, 25, 727), or with potassium iodide and dilute sulphuric acid in presence of vanadyl sulphate (Zeitsch. anal. Chem. 1907, 46, 521). (For other methods, see Amer. J. Sci. 1891, 42, 220 ; J. Amer. Chem. Soc. 1903, 25, 756 ; Zeitsch. anal. Chem. 1907, 46, 308.)

Hypochlorites. A slight excess of $N/10$-sodium arsenite is added and the excess titrated with $N/10$-iodine, or the hypochlorite is directly titrated with the arsenite till a drop of the solution ceases to colour starch-potassium iodide paper blue. As = ClO (Penot's method ; compare Chem. Zeit. 1904, 28, 59).

Perchlorates. The concentrated solution is boiled with a large excess of titanous sulphate, the excess oxidised with permanganate, and the chloride produced is titrated as usual (Zeitsch. anorg. Chem. 1909, 62, 108 ; Chem. Zeit. 1909, 33, 759).

Bromates. The substance is digested at 100° with potassium iodide and concentrated hydrochloric acid in a stoppered bottle, and the liberated iodine titrated with thiosulphate. $BrO_3 = 3I_2$ (compare Zeitsch. anorg. Chem. 1899, 19, 427).

Iodates. These are simply added to a slight excess of potassium iodide solution, acidified with sulphuric or hydrochloric acid, and the liberated iodine titrated. $IO_3 = 3I_2$.

ESTIMATIONS INVOLVING MIXTURES OF THE FOREGOING HALIDE SALTS.

Chloride, Hypochlorite and Chlorate. The solution is titrated with $N/10$-sodium arsenite by Penot's method for the hypochlorite ; the chlorate is then estimated in the solution, after acidifying with sulphuric acid, by reduction with standard ferrous sulphate, and the total chlorine then titrated by Volhard's method (Compt. rend. 1896, 122, 449 ; cf. J. Amer. Chem. Soc. 1909, 31, 525, 1273).

Chloride, Chlorate and Perchlorate. Chloride is titrated in one portion of the solution by Volhard's method, and in another portion after reducing the chlorate with ferrous sulphate. For perchlorate the dry substance, mixed with five times its weight of pure quartz sand and covered with a layer of the same 2 cm. deep, is fused in a platinum crucible for half an hour, cooled, extracted with water, and the total chloride estimated (Compt. rend. 1896, 122, 452).

Chloride and Iodide. The total halogen is titrated by a suitable method in one portion of solution, and the chlorine in another portion after removing iodine by one of the following methods (Amer. J. Sci. 1890, 39, 293). (i.) To the neutral solution (400 c.c.) is added 10 c.c. sulphuric acid (1 : 1), 2 grams ferric sulphate, and 3 c.c. nitric acid, and the whole boiled till all iodine is expelled ; 1 c.c. nitric acid is again added, and the solution again boiled. (ii.) The ferric sulphate and nitric acid of method (i.) are replaced by 2 grams of pure sodium nitrite (or, failing this, by passing into the solution the vapours generated from the slightly impure nitrite and dilute sulphuric acid).

Bromide and Iodide (v. supra, Iodides).

Bromide and Chloride. The solution is acidified so as to contain 25 c.c. of concentrated nitric acid in a total volume of 100 c.c., heated to boiling and boiled for one minute, the source of heat removed and air sucked through the solution until it is perfectly colourless (and for one minute longer). The bromine is then completely expelled ; the residual chloride is titrated by Volhard's method. The total halogens are titrated in another portion of solution (J. Soc. Chem. Ind. 1909, 28, 505).

(For a very accurate but more elaborate method, v. J. Amer. Chem. Soc. 1907, 29, 275 ; also Zeitsch. anorg. Chem. 1895, 10, 387 ; Zeitsch. anal. Chem. 1900, 39, 81.)

Chloride, Bromide, and Iodide. (a) The iodide is decomposed with potassium iodate and acetic acid, the iodide extracted with chloroform and titrated. The bromide is destroyed by boiling with $5N$-nitric acid, any iodate remaining is decomposed with a slight excess of potassium iodide, which excess is readily decomposed by boiling with nitric acid, and the residual chloride

titrated. The total *halogens* are titrated in another portion of solution (J. Amer. Chem. Soc. 1903, 25, 1138).

(b) The *iodide* is destroyed by boiling with ferric sulphate and sulphuric acid, and the amount of ferric salt reduced is determined with $N/10$-dichromate. The *total halogens* are determined by Volhard's method, and, in another portion of solution, the iodide is removed by adding hydrogen peroxide and acetic acid and distilling in steam, the bromine separated as described under *Bromide and Chloride* and the residual *chloride* titrated (J. Soc. Chem. Ind. 1909, 28, 505).

Iron. FERROUS SALTS. *By oxidation.* (a) The cold solution is strongly acidified with dilute sulphuric acid and titrated with $N/10$-permanganate. This simple and accurate method requires modification when hydrochloric acid is present, since it reacts with permanganate. This side-reaction can be practically prevented by adding a moderate quantity of manganese sulphate to the solution and titrating very slowly. A solution is prepared as follows: 67 grams of crystalline manganese sulphate are dissolved in water, 138 c.c. of phosphoric acid (sp.gr. 1·7), and 130 c.c. concentrated sulphuric acid (sp.gr. 1·82) are added, and the mixture diluted to 1 litre. Of this solution, 25 c.c. are added to the ferrous solution to be titrated. The phosphoric acid keeps the ferric solution colourless, and thus facilitates the observation of the end-point (Zeitsch. anal. Chem. 1863, 1, 329; Chem. Zeit. 1889, 13, 323; Amer. Chem. J. 1905, 34, 109; Analyst, 1908, 33, 43, and 1909, 34, 306).

(b) The acid solution is oxidised by $N/10$-dichromate as described under *Preparation of standard solutions.*

FERRIC SALTS. (a) *By reduction* to ferrous salt and titration with permanganate or dichromate. Reduction may be effected in any of the following ways: (i.) The sulphuric acid solution is heated to boiling and hydrogen sulphide passed through it until the solution is completely colourless; the excess of hydrogen sulphide is expelled from the boiling solution by a current of carbon dioxide. (ii.) The nearly neutral solution is boiled with sulphurous acid or ammonium sulphite, excess being removed by continued boiling, preferably in a current of carbon dioxide. (iii.) Eight or ten grams of granulated zinc are added to the warm sulphuric acid solution, and the action allowed to continue until a drop of the solution no longer gives a colouration with potassium thiocyanate. The solution is cooled, filtered through glass wool, and titrated. The use of the zinc-copper couple is preferable (Analyst, 1901, 26, 225; compare Chem. News, 1908, 97, 50). Reduction may be rapidly effected by pouring the liquid through a long column of zinc (The Jones' Reductor (Fig. 15); Chem. News, 1889, 60, 93; Blair's Chemical Analysis of Iron, 6th ed. 94). (iv.) The hydrochloric acid solution is heated nearly to boiling, and stannous chloride (25 p.c. solution) added drop by drop until the solution is colourless; 10 c.c. of saturated mercuric chloride are added to destroy excess of stannous chloride, the solution diluted, manganese sulphate added (*v. supra*), and the ferrous salt titrated with $N/10$-permanganate

(Analyst, 1909, 34, 306). (v.) *Reduction by palladium-hydrogen* in boiling acid solution; this introduces no foreign substance into the
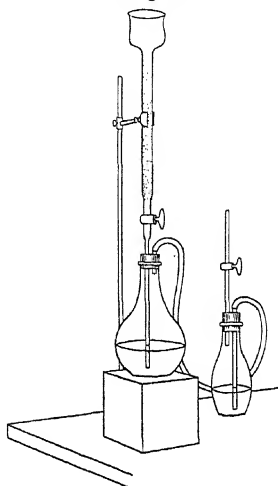
FIG. 15.

solution (Zeitsch. angew. Chem. 1902, 15, 398, 424; Analyst, 1904, 29, 346). (vi.) *Reduction with titanous sulphate* (Amer. J. Sci. 1908, 25, 343).

(b) *By direct titration with a reducing agent.* (i.) *Titanous chloride.* The sulphuric or hydrochloric acid solution of the ferric salt is titrated as described under *Preparation of standard solutions,* p. 205. (ii.) *Stannous chloride.* The nearly boiling hydrochloric acid solution is titrated as described under *Preparation of standard solutions,* p. 205, using either the mercuric chloride indicator (Amer. Chem. J. 1893, 15, 360) or titrating back with iodine.

FERROUS IRON IN MINERALS AND ROCKS. The only satisfactory method consists in decomposing the coarsely powdered substance with sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide, and titrating the ferrous salt produced (*Cooke's Method*; Amer. J. Sci. 1867, 44, 347; *see* also Amer. J. Sci. 1894, 48, 149). The old method of heating with dilute sulphuric acid in a sealed tube (Mitscherlich) is worthless in the presence of sulphur or sulphides (J. Amer. Chem. Soc. 1900, 22, 625). (For an exhaustive discussion of this problem, *v.* Hillebrand's Analysis of Silicate and Carbonate Rocks.)

Iron and Aluminium. After weighing the ignited sesquioxides, they are brought into solution by fusion with potassium hydrogen sulphate or acid potassium fluoride (followed by evaporation with sulphuric acid), and the *iron* reduced and titrated (Zeitsch. angew. Chem. 1905, 18, 815).

Iron and Titanium. Ferric salts can be reduced with sulphurous acid or hydrogen sulphide without reducing *titanic* salts; or reduction of both may be effected with zinc and

sulphuric acid, the *titanous* salt oxidised with a slight excess of bismuth oxide, and the *ferrous* salt titrated in the filtered solution. To estimate both elements present, one of the preceding methods may be combined with the reduction process for titanium, described later, which would give the *total iron and titanium* (*v.* also J. Soc. Chem. Ind. 1909, 28, 189; Analyst, 1910, 35, 198).

Iron and Vanadium. Reduction with sulphur dioxide proceeds with the vanadium as far as to the oxide V_2O_4; reduction with zinc carries it as far as V_2O_2; hence two such reductions and titrations with permanganate furnish data for calculating both iron and vanadium (Amer. J. Sci. 1908, 26, 79).

Lead. *By precipitation* (i.) *As molybdate.* The boiling acetic acid solution is titrated with standard ammonium molybdate (4·75 grams per litre, titrated against pure lead) until a drop of solution gives a brown or yellow colour with a drop of dilute tannic acid solution. The indicator not being very sensitive, a 'blank' experiment should be made and the necessary correction allowed for both in an assay and in standardising the solution. (ii.) *As ferrocyanide.* The cold acetic acid solution is titrated with potassium ferrocyanide (10 grams per litre titrated against pure lead) until a drop of the solution produces a brown colouration with a drop of saturated uranium acetate solution; a 'blank' experiment should also be made (J. Amer. Chem. Soc. 15, 550; Chem. News, 1896, 73, 18). In determining lead in ores, &c., it is usually separated as sulphate and dissolved in ammonium acetate previous to titration. (For a comprehensive review of methods for lead, *v.* Chem. News, 1903, 87, 40; Gaz. chim. ital. 1896, 26, i. 327; *see also Methods of separation*; and J. Amer. Chem. Soc. 1903, 25, 632; 1904, 26, 1135.)

Magnesium. (*a*) *Acidimetrically.* The magnesium is precipitated as the double ammonium phosphate, the precipitate washed with dilute ammonia, and then with aqueous alcohol till free from extraneous ammonia, dissolved in a measured excess of $N/10$-hydrochloric acid, and the excess titrated with $N/10$-sodium hydroxide, using methyl orange for indicator:

$$Mg(NH_4)PO_4 + 2HCl = MgCl_2 + H_2(NH_4)PO_4$$
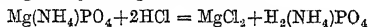
(Chem. Zentr. 1876, 727; for a method which obviates the use of alcohol, *v.* J. Amer. Chem. Soc. 1900, 22, 31; *see also Phosphorus*).

(*b*) *Iodimetrically.* The magnesium is precipitated as double ammonium arsenate, dissolved in hydrochloric acid and potassium iodide, and the iodine titrated (J. Amer. Chem. Soc. 1899, 21, 746; Zeitsch. anal. Chem. 1907, 46, 714).

Manganese. (*a*) *By oxidation with permanganate.* (*Volhard's method, modified.*) The neutral chloride or sulphate solution containing 10 grams of zinc sulphate is heated to boiling, 1 gram of freshly ignited zinc oxide added, and the liquid titrated with $N/10$-permanganate, boiling and shaking frequently until the supernatant liquid is red; 1 c.c. pure glacial acetic acid is added, and the titration slowly finished with permanganate in the hot *but not boiling* liquid. The manganese can be accurately calculated from the equation:

$$3MnO + Mn_2O_7 = 5MnO_2$$
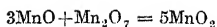
(Zeitsch. anal. Chem. 1909, 48, 751; Little and Cahen, Analyst, 1911, 36, 52).

(*b*) *By precipitation as dioxide* and estimation of the available oxygen. Precipitation may be effected in one of the following ways: (i.) By adding bleaching-powder solution and calcium carbonate to a hot neutral solution of the manganese salt containing ferric and zinc chlorides (Chem. Soc. Trans. 1879, 35, 365; J. Soc. Chem. Ind. 1891, 10, 333). (ii.) By boiling the solution in concentrated nitric acid (quite free from any hydrochloric acid) with potassium (or preferably sodium) chlorate. (iii.) By boiling the dilute sulphuric acid solution with ammonium persulphate (Zeitsch. angew. Chem. 1901, 14, 1149; 1903, 16, 905; Compt. rend. 1902, 135, 965; 1903, 136, 449). The washed precipitate in either case is dissolved in a sulphuric acid solution of standard ferrous sulphate or oxalic acid, and the excess of reagent titrated. The precipitate obtained by method (ii.) is deficient in available oxygen (Amer. J. Sci. 1898, 5, 260), and the standard solution employed in the final titration must therefore be standardised on a known amount of manganese treated in a similar fashion.

(*c*) *By conversion into permanganic acid.* (i.) The cold solution free from hydrochloric acid, and containing one quarter its volume of nitric acid (specific gravity 1·42), is oxidised by shaking with 2–4 grams of sodium bismuthate for three minutes, diluted with half its volume of 3 p.c. nitric acid, the solid residue allowed to settle, and the permanganic acid solution filtered into a slight excess of ferrous sulphate; excess of the latter is then titrated with $N/10$-permanganate (Dingl. poly. J. 269, 224; Chem. Soc. Trans. 1895, 67, 268; Chem. News, 1901, 84, 209, 247; J. Amer. Chem. Soc. 1904, 26, 793). (ii.) The oxidation of small quantities of manganese may be effected by boiling the nitric acid solution with lead peroxide, or by heating with ammonium persulphate in the presence of a little silver nitrate (Chem. News, 1901, 84, 239).

Manganese in Ferromanganese and Steels. The foregoing methods *a, b,* and *c* (i.) have all been employed for this purpose; method *c* (i.) is the simplest and probably the most accurate. In method *a* it is necessary to remove iron from the solution; this is conveniently performed by adding a slight excess of zinc oxide to the solution (*v.* references given above; also J. Amer. Chem. Soc. 1902, 24, 243; Ann. Chim. anal. 1906, 11, 124).

Manganese and Chromium occurring together in steels may be estimated by oxidising with ammonium persulphate in sulphuric acid solution in the presence of silver nitrate; one portion of solution is titrated for total permanganate and chromate with ferrous sulphate, and another for permanganate alone by means of arsenious oxide (J. Amer. Chem. Soc. 1905, 27, 1550; *v.* also Chem. News, 1901, 83, 25; 1905, 91, 3; Chem. Zeit. 1905, 29, 987; Chem. Zeit. Rep. 1905, 29, 380).

The foregoing bismuthate method *c* (i.) may be applied in the presence of *molybdenum, tungsten, titanium,* and *vanadium*; also, with certain precautions, in the presence of *chromium* (Chem. News, 1901, 84, 247). (For estimating *manganese*

in *tungsten steels, v.* also J. Soc. Chem. Ind. 1907, 26, 345.)

Mercury. (*a*) *By precipitation.* Mercuric nitrate is readily titrated with $N/10$-thiocyanate, using ferric nitrate as indicator, provided that nitric acid is present in fairly high concentration (Ber. 1901, 34, 3502 ; 1902, 35, 2015). Chloride must be absent ; if necessary, the mercury is precipitated as oxide with sodium hydroxide, and the washed precipitate dissolved in nitric acid.

(*b*) *Iodimetrically.* The mercuric solution (25–50 c.c.) containing 1 gram of potassium iodide is made alkaline with sodium hydroxide, 2–3 c.c. of 40 p.c. formaldehyde added, and the whole shaken vigorously for two minutes. The solution is acidified with acetic acid, and the reduced mercury is dissolved by adding an excess of $N/10$-iodine. After shaking, the excess of iodine above that required to form mercuric iodide is titrated with $N/10$-thiosulphate (Ber. 1906, 39, 3702 ; 1907, 40, 3276 ; Bull. Soc. chim. 1907, [iv.] 1, 1169). Mercurous salts require a preliminary oxidation.

(For other methods, *v.* Compt. rend. 1863, 56, 63 ; Chem. Soc. Trans. 1892, 61, 364 ; Arch. Pharm. 241, 444.)

Molybdenum. (*a*) *By reduction and subsequent oxidation.* The sulphuric acid solution is reduced by passing it through a long column of amalgamated zinc to a condition represented by the formula Mo_2O_3 ; the liquid is caught directly in ferric sulphate solution, which re-oxidises the molybdenum salt, and the ferrous sulphate produced is titrated with $N/10$-permanganate (Amer. J. Sci. 1907, 24, 313 ; compare Ber. 1905, 38, 604 ; Analyst, 1907, 32, 250).

(*b*) *Iodimetrically.* The solution in concentrated hydrochloric acid is boiled with a slight excess of potassium iodide till the volume is reduced to 25 c.c., when complete reduction to the condition Mo_2O_5 is effected. The solution is cooled, diluted to 125 c.c., 0·5 gram of manganese sulphate added, and then a slight excess of $N/10$-permanganate ; $N/10$-arsenious acid is next added, and after the addition of tartaric acid and sodium bicarbonate, the excess is titrated with $N/10$-iodine. The permanganate *plus* iodine and *minus* the arsenious acid measure the Mo_2O_5 present (Amer. J. Sci. 1901, 12, 449 ; compare *ibid.* 1896, 2, 156 ; 1898, 6, 168).

Molybdenum in Steels and Alloys (v. J. Amer. Chem. Soc. 1904, 26, 675).

Nickel. (*a*) *By double cyanide formation.* A few drops of 10 p.c. potassium iodide are added to the cold, slightly ammoniacal nickel solution, and then a small measured volume of silver nitrate (3 grams of silver per litre). Standard potassium cyanide (25 grams per litre) is then run in with stirring till the precipitate of silver iodide just disappears ; more silver nitrate is added till a very faint turbidity is produced, which is then dissolved by the least possible excess of cyanide. The relative values of the silver nitrate and cyanide solutions are determined by a preliminary experiment, and the cyanide standardised against a known amount of pure nickel (or pure silver, and calculated to nickel). The method is rapid and accurate (Chem. News, 1895, 72, 92).

(*b*) *By precipitation.* The hot nickel solution containing ferric chloride and citric acid

is made feebly ammoniacal and titrated slowly, stirring constantly, with standard potassium ferrocyanide (20 grams per litre, titrated against pure nickel), until a drop of the solution when acidified with dilute acetic acid develops a green colour in five minutes (J. Amer. Chem. Soc. 1910, 32, 757 ; Bull. Soc. chim. 1907, 4, 1163).

Nickel in Steel. Method (*b*) can be directly applied ; method (*a*) can also be employed without removing iron, molybdenum, or chromium, if a sufficient excess of ammonium citrate or sodium pyrophosphate is added to the solution ; or a moderate amount (2–3 grams) of each of these reagents may be added (J. Amer. Chem. Soc. 1907, 29, 1201 ; 1908, 30, 1116 ; 1899, 21, 854 ; Chem. Zeit. 1908, 32, 1223). (For modifications in presence of other metals, *v.* Chem. News, 1898, 78, 177, 190.)

Nitrogen. AMMONIA (*v.* ACIDIMETRY AND ALKALIMETRY).

HYDRAZINE. *Iodimetrically.* A moderate excess of sodium bicarbonate or sodium acetate is added to the solution of a hydrazine salt, which is then titrated with $N/10$-iodine. $N_2H_4=21$ (J. pr. Chem. 1902, 66, 332 ; 1903, 67, 140 ; *v.* also Gazz. chim. ital. 1899, 29, 265).

HYDROXYLAMINE. (*a*) *By oxidation.* The solution of a hydroxylamine salt is slowly added to excess of boiling and well stirred Fehling's solution, the precipitated cuprous oxide washed, dissolved in acid ferric alum, and the ferrous salt titrated with permanganate. $NH_2OH=Cu_2$ (Chem. Soc. Trans. 1903, 83, 1394 ; compare Ber. 1877, 10, 1940).

(*b*) *By reduction.* An excess of titanium sesquisulphate is added to the acid solution, and the ammonium salt produced is estimated by distillation with sodium hydroxide (Ber. 1909, 42, 2695).

NITRATES. (*a*) *By reduction.* The solution is made strongly alkaline with sodium hydroxide, 5 c.c. of alcohol and 2·5–3 grams of powdered Devarda's alloy added, and the flask connected with a distilling apparatus, the receiver of which contains excess of $N/2$-hydrochloric acid. After standing for half an hour, the liquid is steam-distilled for an equal length of time, when all the nitrate has been converted into ammonia and driven over into the acid ; the excess of the latter is then titrated (Zeitsch. anal. Chem. 1894, 33, 113 ; Analyst, 1910, 35, 307 ; *v.* also the *Gravimetric section*).

(*b*) *Iodimetrically (v.* Zeitsch. angew. Chem. 1890, 3, 477 ; Chem. Soc. Trans. 1891, 59, 530 ; Amer. J. Sci. 1892, 44, 117).

NITRITES. (*a*) *By oxidation.* The nitrite solution is slowly added to a measured quantity of $N/10$-permanganate, which is acidified with sulphuric acid, diluted to 400 c.c., and warmed to 40°, until the colour is just discharged. $2HNO_2 = O_2$. Otherwise, the cold dilute nitrite solution is slowly titrated with $N/10$-permanganate to a red colouration ; a few drops of sulphuric acid are then added, followed by an excess of permanganate. The liquid is then strongly acidified with sulphuric acid, heated nearly to boiling, and the excess of permanganate titrated with $N/10$-oxalic acid (Amer. Chem. J. 1883, 5, 388).

(*b*) *Iodimetrically.* Several methods have been based on the reaction.

$$2HI+2HNO_2 = I_2+2NO+2H_2O.$$
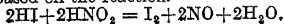
It is necessary to perform the experiment in an atmosphere free from oxygen; the iodine may be determined by thiosulphate or arsenite. (For details, v. Pharm. J. 19, 741; Chem. News, 1904, 90, 114; cf. *Organic analysis*, Aromatic amines.)

Osmium. *Iodinetrically* (v. Chem. Zentr. 1898, ii. 65).

Oxygen. PEROXIDES. (a) *Iodimetrically.* Such peroxides as those of manganese and lead may be estimated by distillation with concentrated hydrochloric acid, and collecting the chlorine evolved in potassium iodide (*Bunsen's method*). Finely divided peroxides of manganese react quantitatively with cold dilute hydrochloric acid and potassium iodide (Chem. Soc. Trans. 1880, 37, 128), a method of estimation that is available with the peroxides of the alkali and alkali earth metals, which do not give satisfactory results by the distillation method (Arch. Pharm. 1902, 240, 437). Hydrogen peroxide may be determined in this manner (Analyst, 1888, 13, 62).

(b) *By reduction.* Hydrogen peroxide, or peroxides of the alkal and alkaline-earth metals, may be estimated in cold dilute acid and titrated with $N/10$-permanganate, which loses as much oxygen as is lost by the peroxide (v. also *Gas-Volumetric methods*).

(For critical reviews of methods, &c., v. Arch. Pharm. 228, 432; Amer. Chem. J. 1906, 36, 117; Zeitsch. angew. Chem. 1901, 14, 828; 1908, 21, 589; Chem. Zeit. 1906, 30, 1275; 1907, 31, 1257; Zeitsch. anal. Chem. 1908, 47, 465.)

Phosphorus. PHOSPHORIC ACID (ORTHO-). (a) v. ACIDIMETRY AND ALKALIMETRY.

(b) *Acidimetrically, with previous precipitation.* (i.) The precipitated magnesium ammonium phosphate (v. *Gravimetric section*) is washed and titrated as described under *Magnesium*, p. 212 (Zeitsch. anal. Chem. 1898, 37, 217; Zeitsch. angew. Chem. 1905, 18, 655; compare Zeitsch. anal. Chem. 34, 33). (ii.) The precipitate of ammonium phosphomolybdate (v. *Gravimetric section*) after washing is dissolved in a slight excess of standard potassium hydroxide free from carbonate, and the excess titrated with standard nitric acid using phenolphthaleïn as indicator. One molecular proportion of P_2O_5 present as $(NH_4)_3PO_4,12MoO_3$, requires 23 molecules of K_2O in pure aqueous caustic potash. $P_2O_5=23K_2O$ (J. Amer. Chem. Soc. 1895, 17, 950; 1897, 19, 703; J. Soc. Chem. Ind. 1904, 23, 1186).

(c) *By precipitation.* To the solution, feebly acid with acetic acid, 10 c.c. of 10 p.c. ammonium acetate are added and standard uranium acetate solution (35 grams per litre) run in from a burette until a drop of the solution gives a brown colouration with potassium ferrocyanide upon a white tile. The solution is heated to boiling, when the latter reaction will no longer take place, and more uranium acetate added until the brown colouration is obtained once more, e.g.:

$$KH_2PO_4+UO_2(C_2H_3O_2)_2+NH_4\cdot C_2H_3O_2$$
$$= KC_2H_3O_2+2HC_2H_3O_2+UO_2NH_4PO_4$$
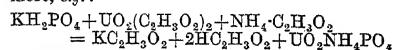
In analysing alkali phosphates, the uranium solution is standardised against pure potassium dihydrogen phosphate, while a solution of calcium phosphate in acetic acid, standardised gravimetrically by the method of Woy (Chem. Zeit. 1897, 21, 442), must be used if the uranium acetate is to be used for estimating phosphates of the alkaline earths (J. Soc. Chem. Ind. 1892, 11, 328). It is essential that titrations should be made under conditions closely approximating those which obtained when the uranium solution was standardised.

PHOSPHORUS IN IRON AND STEEL. This is usually separated as ammonium phosphomolybdate; it may then be titrated according to b (ii.) above, or the precipitate is washed with dilute ammonium sulphate, dissolved in ammonia, the solution strongly acidified with sulphuric acid, reduced with zinc, and the Mo_2O_3 solution collected directly in ferric alum, the ferrous salt being then titrated as described under *Molybdenum* (Amer. J. Sci. 1907, 24, 313; compare Blair's Analysis of Iron).

Potassium. *By oxidation.* The acetic acid solution, free from ammonium salts, is evaporated on the water-bath till pasty with sodium cobaltinitrite solution in rather large excess, cooled and stirred with 50–100 c.c. of cold water. The dipotassium sodium cobaltinitrite is collected, on asbestos, washed with cold water, and then immersed in an excess of nearly boiling permanganate solution. After 5 minutes the solution is acidified with sulphuric acid, excess of $N/10$-oxalic acid added, and the clear solution titrated with permanganate. The permanganate is best standardised against a pure potassium salt. The oxidation of 2 molecular proportions of $K_2NaCo(NO_2)_6$ by permanganate requires 11 atomic proportions of oxygen or $4K = 22H$ (Amer. J. Sci. 1907, 24, 433; compare Chem. Soc. Trans. 1900, 77, 1076). (For another method, v. Chem. Zeit. 1895, 19, 301.)

Selenium. SELENIOUS ACID. *By oxidation.* To the cold solution containing 5 p.c. by volume of concentrated sulphuric acid is added an excess of $N/10$-permanganate; a moderate excess of $N/10$-oxalic acid is then added, and the titration finished at 50°–60° with permanganate. $2SeO_2 = O_2$ (Amer. J. Sci. 1895, 50, 51).

(For an entirely different method, v. Amer. Chem. J. 1896, 18, 703; Amer. J. Sci. 1899, 7, 287.)

SELENIC ACID. *Iodinetrically.* (i.) The acid is boiled with hydrochloric acid (25 c.c. concentrated acid in a total volume of 75 c.c.) for 10 minutes in a Bunsen distilling apparatus or one of its various modifications, and the chlorine evolved is collected in potassium iodide (v. supra, *Volumetric estimation of halogens*, p. 209) $SeO_3 = Cl_2$ (Amer. J. Sci. 1895, 50, 400). (ii.) The solution (60 c.c.) containing 20 c.c. of sulphuric acid (1:1) and 1 gram of potassium bromide is distilled and the liberated bromine collected in potassium iodide. $SeO_3 = Br_2$ (Amer. J. Sci. 1895, 50, 402).

SELENIUM IN EITHER STATE OF OXIDATION. *Iodinetrically.* This is effected by a Bunsen distillation, the solution (60 c.c.) containing 5 c.c. of concentrated hydrochloric acid and 1–3 grams of potassium iodide. The selenium compound is reduced to the element itself, and an equivalent of iodine is distilled into potassium iodide and titrated. $SeO_2 = 2I_2$ and $SeO_3=3I_2$ (Amer. J. Sci. 1895, 50, 249; for a simpler method v. Amer. J. Sci. 1896, 1, 31).

Silver. *By precipitation.* (i.) The nitric acid solution is titrated with standard sodium chloride until no further precipitation is observed. (For details of this very exact method, *v.* the article on ASSAYING.) A number of devices have been described for rapidly filtering a portion of the liquid in order to test it for further precipitation (Chem. Soc. Trans. 1908, 93, 1037 ; Gazz. chim. ital. 1909, 39, ii. 240). A modified method consists in adding a slight deficit of sodium chloride, filtering and titrating the remaining silver with dilute ammonium thiocyanate (J. Amer. Chem. Soc. 1897, 19, 814 ; *v.* also Chem. Soc. Trans. 1900, 77, 232 ; Zeitsch. angew. Chem. 1904, 17, 647). (ii.) Titration may be effected with $N/10$-thiocyanate as described under *Preparation of standard solutions.*

Sodium (*v.* Chem. Soc. Trans. 1898, 73, 167).

Sulphur, Acids of. HYDROGEN SULPHIDE. *Iodimetrically.* The gas or a measured volume of solution is absorbed in an excess of $N/10$-iodine, the excess being afterwards titrated with $N/10$-thiosulphate. $H_2S = I_2$. Direct titration with iodine leads to low results (Zeitsch. anal. Chem. 1906, 45, 541).

HYDROSULPHUROUS ACID. *By oxidation.* The sodium salt, used in indigo-dyeing, can be estimated by dissolving it in air-free water in an atmosphere of carbon dioxide, adding a drop of ferrous sulphate, and running in standard potassium ferricyanide solution until a blue colour appears, air being rigidly excluded (Zeitsch. angew. Chem. 1905, 18, 168) :

$$Na_2S_2O_4 + 2K_3Fe(CN)_6 = 2SO_2 + 2K_3NaFe(CN)_6.$$
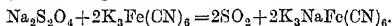
If necessary, a little acetic acid is added to ensure that the liquid shall be acid.

SULPHUROUS ACID. *Iodimetrically.* An aqueous solution of sulphur dioxide is estimated by running it into an excess of standard iodine solution with constant stirring, and not *vice versâ*, since that method causes a separation of sulphur due to the side-reaction :

$$SO_2 + 4HI = S + 2H_2O + 2I_2$$
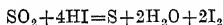
(Annalen, 1887, 242, 94). Sulphites may be accurately determined by adding the powdered salt to excess of $N/10$-iodine, and after the decomposition is complete, titrating back with $N/10$-thiosulphate (J. Soc. Chem. Ind. 1884, 3, 197 ; 1885, 4, 303)

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$
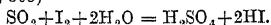
SULPHURIC ACID. (*a*) *Iodimetrically.* The feebly acid boiling dilute sulphate solution is precipitated with an excess of a solution of barium chromate in hydrochloric acid (3–4 grams $BaCrO_4$, 30 c.c. conc. HCl, diluted to 1 litre). Barium sulphate is thus precipitated, and an equivalent of chromic acid liberated. The boiling solution is neutralised with powdered chalk to remove excess of barium chromate, and the chromic acid in the cold filtrate titrated iodimetrically. $CrO_3 = SO_3$ (Amer. Chem. J. 1889, 11, 567 ; Chem. Zeit. 1898, 22, 357).

(*b*) *By precipitation.* (i.) The boiling sulphate solution, slightly acid with hydrochloric acid, is titrated with standard barium chloride until no more precipitate is produced. $Ba = SO_4$ (Chem. News, 1889, 59, 41). A device for readily observing the end-point is described in Chem. Soc. Trans. 1907, 91, 1370. (ii.) Method (i.) may be modified by adding an excess of

barium chloride, and determining the excess by adding sodium acetate, acetic acid, and ammonium dichromate, and titrating an aliquot part of the filtrate with $N/20$-ferrous sulphate (Chem. Soc. Trans. 1909, 95, 2198). (iii.) The sulphate is precipitated from dilute solution with excess of benzidine hydrochloride solution as benzidine sulphate, and the precipitate titrated with $N/10$-sodium hydroxide, using methyl orange as indicator (*v.* Zeitsch. angew. Chem. 1907, 20, 9, for details, corrections, &c.).

THIOSULPHURIC ACID. *Iodimetrically.* Thiosulphates are titrated with iodine as in standardising thiosulphate solution (*v. supra,* p. 205) ; sparingly soluble salts are suspended in water and titrated, shaking vigorously in a stoppered bottle all the time.

PERSULPHURIC ACID. (*a*) *By oxidation.* The solution is acidified with sulphuric acid, a considerable excess of standard ferrous sulphate is added, and then 100 c.c. of hot distilled water (70°–80°). Excess of ferrous salt is then quickly titrated with $N/10$-permanganate. $H_2S_2O_8 = 2FeO$ (Chem. Soc. Abst. 1900, ii. 45).

(For other methods, *v.* Chem. Zentr. 1900, 435 ; Amer. J. Sci. 1901, 12, 367 ; Gazz. chim. ital. 1902, 32, ii. 383 ; Bull. Soc. chim. 1903, 30, 930.)

Tellurium. TELLUROUS COMPOUNDS. (*a*) *By oxidation.* The solution is rendered alkaline with sodium hydroxide, an excess of $N/10$-permanganate is added, and the excess destroyed by acidifying with sulphuric acid, adding $N/10$-oxalic acid in excess, and finishing the titration with permanganate. $2TeO_2 = O_2$ (Chem. Soc. Trans. 1891, 59, 238 ; Amer. J. Sci. 1899, 8, 122).

(*b*) *By precipitation* as tetraiodide in moderately concentrated sulphuric acid solution (Amer. J. Sci. 1896, 2, 271).

(*c*) *Iodimetrically* (*v.* Amer. Chem. J. 1898, 20, 278).

TELLURIC COMPOUNDS. *Iodimetrically.* The tellurate is distilled with concentrated hydrochloric acid in Bunsen's apparatus, the chlorine absorbed in potassium iodide and the iodine set free is titrated with $N/10$-thiosulphate. Telluric anhydride must be previously dissolved in concentrated potassium (not sodium) hydroxide, since it is scarcely attacked by hydrochloric acid. The reduction, which proceeds to tellurous acid, may be also effected by distilling with potassium bromide and dilute sulphuric acid (Zeitsch. anorg. Chem. 1894, 7, 132).

Thallium. *Iodimetrically.* The dilute solution of thallic salt is mixed with excess of potassium iodide, and the iodine liberated is titrated with $N/10$-thiosulphate. $Tl = I_2$ (Compt. rend. 1902, 134, 655).

Tin. STANNOUS SALTS. *Iodimetrically.* The cold hydrochloric acid solution of the stannous salt is titrated with $N/10$-iodine. $Sn = I_2$ (J. Amer. Chem. Soc. 1897, 19, 809). Free exposure of the solution to air must be avoided, since stannous salts readily undergo oxidation ; it is preferable to work in an atmosphere of carbon dioxide.

STANNIC SALTS must be reduced before titration with iodine ; this may be accomplished by heating the hydrochloric acid solution with iron, or sheet nickel, or with finely powdered antimony (Chem. News, 1901, 84, 167).

Titanium. *By reduction and subsequent oxidation.* It is difficult to obtain accurate results with quantities of titanium dioxide exceeding 0·15 gram. The warm, dilute sulphuric acid solution of titanic salt is reduced to the tervalent condition by means of zinc, aluminium-magnesium alloy, or zinc-aluminium alloy (Zn, 90 p.c. Al 10 p.c., cast in sticks), cooled and rapidly filtered into ferric sulphate solution; the equivalent quantity of ferrous sulphate produced is titrated with $N/10$-permanganate. Ti = Fe (Chem. Zeit. 1907, 31, 399; Amer. J. Sci. 1908, 25, 130; Analyst, 1910, 35, 198; compare J. Amer. Chem. Soc. 1895, 17, 878).

Titanium and Iron (v. Iron).

Tungsten. *By reduction and subsequent oxidation.* The solution is reduced by zinc and hydrochloric acid to a condition corresponding to the oxide WO_2, filtered and titrated with a standard ferric solution. The end-point is perceived by the disappearance of the intense blue colour of the intermediate compound corresponding to W_2O_5, the reaction

$$Fe_2O_3 + WO_2 = WO_3 + 2FeO$$
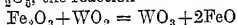
being quantitative (Chem. Soc. Proc. 1909, 25, 227).

Uranium. *(a) By reduction and subsequent oxidation.* The solution, containing 20 c.c. of concentrated sulphuric acid in a volume of 125 c.c., is poured upon 100 grams of pure zinc (in sticks 2 cm. long), heated nearly to boiling for 15 minutes, filtered into a large porcelain dish, and the zinc washed with cold dilute sulphuric acid (1 : 10 by volume) till the total volume of solution is 300 c.c. The solution of uranous sulphate, which should be sea-green in colour, is then titrated with $N/10$-permanganate. The solution can also be reduced by passage through a long column of amalgamated zinc; in either case the reduction proceeds a little too far, but oxidation to the uranous state is accomplished during the filtration and washing. High results are obtained by carrying out the experiment in an atmosphere of carbon dioxide.

$$5U(SO_4)_2 = 2KMnO_4 = 10FeSO_4, \text{ or } U = 2Fe$$

(J. Amer. Chem. Soc., 1909, 31, 367; compare *ibid.* 1901, 23, 685; 1906, 28, 1541; Amer. J. Sci. 1903, 16, 229).

(b) Iodimetrically (v. Ber. 1904, 37, 189).

Uranium and Vanadium (v. J. Amer. Chem. Soc. 1906, 28, 1443).

Vanadium. *(a) By reduction and subsequent oxidation.* (i.) The vanadic solution containing sulphuric acid is boiled with sulphur dioxide until the colour is a pure blue, and the excess of sulphur dioxide then expelled with carbon dioxide; the solution, containing vanadium salt corresponding to the oxide V_2O_4, is then titrated hot with $N/10$-permanganate. (ii.) The sulphuric acid solution is passed through a long column of amalgamated zinc, and the reduced solution collected and titrated as described under *Molybdenum (v. supra,* p. 213). In this case reduction proceeds as far as the oxide V_2O_2 (Amer. J. Sci. 1908, 25, 332; compare *ibid.* 1903, 15, 389). (iii.) The solution is evaporated nearly to dryness three times with concentrated hydrochloric acid, when vanadyl chloride $VOCl_2$ is formed; hydrochloric acid is removed by evaporation with sulphuric acid, the solution

diluted and titrated with $N/10$-permanganate Ber. 1903, 36, 3164).

(b) By reduction. The vanadate solution, hot or cold, and containing hydrochloric or sulphuric acid, is titrated with standard (2 p.c.) stannous chloride (titrated against iodine) until a drop of the solution gives a blue colouration with ammonium molybdate. Reduction proceeds as far as the tetroxide V_2O_4 (Bull. Soc. chim. 1908, 3, 626).

(c) Iodimetrically. (i.) About 0·3–0·5 gram of vanadate is distilled with 1·5–2·0 grams of potassium bromide and 30 c.c. of concentrated hydrochloric acid, the liberated bromine absorbed in potassium iodide, and the iodine titrated with $N/10$-thiosulphate; $V_2O_5 = Br_2$, the reduction proceeding to the tetroxide (Chem. Zentr. 1890, i. 977; for other iodimetric methods, *v.* Amer. J. Sci. 1896, 2, 185, 355; 1902, 14, 369).

Vanadium and Chromium (v. Bull. Soc. chim. 1904, 31, 962).

Vanadium and Uranium (v. J. Amer. Chem. Soc. 1906, 28, 1443).

Vanadium and Iron (v. Iron; and J. Amer. Chem. Soc. 1908, 30, 1229, 1233).

Zinc. *(a) By precipitation.* The chloride solution, containing 3 c.c. of concentrated hydrochloric acid in a volume of 250 c.c., is heated nearly to boiling, and titrated with standard potassium ferrocyanide solution (21·5 grams per litre, titrated against pure zinc) until one or two drops of the solution produce a brown colouration with uranium nitrate (J. Amer. Chem. Soc. 1900, 22, 198; 1904, 26, 4; 1908, 30, 225; Zeitsch. anal. Chem. 1906, 44, 174). The uranium nitrate indicator may be replaced by ammonium molybdate (Chem. Zeit. 1905, 29, 951). It has been recommended to add excess of ferrocyanide, and titrate back with standard zinc chloride (Zeitsch. anal. Chem. 1896, 35, 460).

(For the application of this method to ores and alloys, *v.* J. Amer. Chem. Soc. 1907, 29, 265; Chem. Zeit. 1905, 29, 951; J. Soc. Chem. Ind. 1905, 24, 228, 1278.)

(b) Acidimetrically. As for *Magnesium, v. supra,* p. 212; and J. Amer. Chem. Soc. 1901, 23, 468.

(c) Iodimetrically. As for *Magnesium, v. supra,* p. 212; and J. Amer. Chem. Soc. 1900, 22, 353.

COLORIMETRIC METHODS.

These methods are especially valuable for the estimation of very small quantities of substances, and are capable of giving very accurate results. The depth of tint produced by some characteristic colour reagent in a given volume of the solution is compared with the tint produced by the same reagent in an equal volume of a solution containing a known quantity of the substance to be determined. The tint in the comparison tube can be varied by varying the proportion of the substance which it contains, and when the tints are equal the quantities of the substance in each tube are also equal. The quantity in one tube is known, and hence that in the other is determined. It is important that the comparison be made under comparable conditions with respect to degree of acidity or alkalinity, proportion of the reagent, and the

like. It is also important that the depth of tint should not be materially affected by the presence of other saline substances in the solution under examination.

The following substances may be determined by these methods :—

Lead, with hydrogen sulphide.

Copper, with hydrogen sulphide or potassium ferrocyanide (Carnelley, Chem. News, 32, 308).

Iron, with potassium ferrocyanide (Carnelley, Chem. News, 30, 257).

Iron, with potassium thiocyanate (Thomson, Chem. Soc. Trans. 1885, 493).

Vanadium, with hydrogen peroxide.

Titanium, with hydrogen peroxide (Weller, Ber. 1882, 15, 2593).

Ammonia, by Nessler's solution (v. WATER).

Iodine, in solution in carbon disulphide, or with starch.

Nitrates, by phenolsulphonic acid test (v. WATER).

Nitrites, by (i.) m-phenylenediamine ; (ii.) sulphanilic acid and α-naphthylamine (v. WATER).

The principle may likewise be applied to the comparison of colouring matters, provided that the solutions are sufficiently diluted (v. COLORI-METER).

ULTIMATE ANALYSIS OF CARBON COMPOUNDS.

The majority of carbon compounds contain carbon, hydrogen, and oxygen, or carbon, hydrogen, oxygen, and nitrogen ; a smaller number contain one or more of the halogens, or sulphur. There are a still smaller number of organic derivatives of phosphorus, arsenic, antimony, silicon, and other metalloidal and metallic elements, and the metals also occur in the salts of organic acids.

Qualitative Examination.

Carbon is converted into carbon dioxide when the substance is heated with cupric oxide.

Hydrogen. The substance is heated to a temperature below that at which decomposition begins, until all water existing as such is expelled, and is then heated with finely divided and recently ignited cupric oxide ; the hydrogen is evolved as water.

Nitrogen. Many carbon compounds containing nitrogen evolve this element in the form of ammonia when heated with caustic soda or soda-lime, but this test is not applicable to nitro-, nitroso-, azo-, and diazo- derivatives.

Many nitro-, nitroso-, and diazo- derivatives evolve oxides of nitrogen, with or without explosion, when heated.

Nitrogen in all classes of carbon compounds, with the exception of the diazo- compounds, may be detected by heating the substance with metallic sodium or potassium, together with some sodium carbonate if the substance is explosive. The nitrogen is converted into alkali cyanide, and the cooled mass is extracted with water and the cyanogen detected by the Prussian-blue test, which consists in adding ferrous sulphate to the alkaline solution after filtration, warming gently and then acidifying. Nitrogenous carbon compounds containing sulphur yield, when heated with sodium, a thiocyanate, and the Prussian-blue test cannot be used. A large excess of potassium is recommended in this case, when it is stated that sulphur

does not interfere (Täuber, Ber. 1899, 32, 3150). A mixture of potassium carbonate (138 parts) and magnesium powder (72 parts) has been recommended for general use in detecting nitrogen even in the case of diazo- derivatives and stable pyrrole compounds (v. Ber. 1902, 35, 2523 ; Gazz. chim. ital. 1904, 34, [2] 359). This mixture is, however, found to take up nitrogen from the atmosphere (Ellis, Chem. News, 1910, 102, 187).

Halogens are detected by heating the substance with pure lime or pure soda-lime, extracting with water, slightly acidifying with nitric acid, and testing with silver nitrate. Highly nitrogenous compounds, when heated with lime, are apt to yield calcium cyanide ; hence the supposed precipitate of silver halide should always be tested for cyanide (v. Separation of cyanide and chloride), unless nitrogen is known to be absent. With soda-lime no cyanide is formed. The substance may also be heated with sodium or potassium as in testing for nitrogen ; iodine and bromine are detected by acidifying, adding chlorine water, and shaking up with chloroform, which becomes purple or brown. The supposed silver chloride should, however, always be tested for cyanide.

Sulphur and phosphorus in non-volatile substances are detected by fusing with caustic soda or potash mixed with about one-fifth its weight of potassium nitrate, or by heating with sodium peroxide diluted with sodium carbonate ; in either case the product is tested for sulphuric or phosphoric acid. Volatile or non-volatile substances may be oxidised by heating in a sealed tube at 150°–300°, according to circumstances, with fuming nitric acid of sp.gr. 1·5. Sulphur and phosphorus are oxidised to sulphuric and phosphoric acid respectively.

Sulphur is also detected by heating the substance with sodium, extracting with water, and adding sodium nitroprusside, when a brilliant violet colouration indicates the presence of alkaline sulphide.

Arsenic and antimony are detected by fusing the substance with equal weights of sodium carbonate and sodium peroxide, extracting with water, acidifying, and passing in hydrogen sulphide. Other appropriate tests for these two elements may be applied.

Quantitative Determinations.

Carbon and hydrogen in absence of nitrogen, halogens, &c.

The simplest and most convenient method for general purposes is to burn the compound in a glass tube in a current of oxygen, assisted by cupric oxide ; the carbon is converted into carbon dioxide, which is absorbed by caustic potash ; the hydrogen is converted into water, which is absorbed by calcium chloride or concentrated sulphuric acid.

Erlenmeyer's modification of Von Babo's furnace is frequently employed. The heat is supplied by a row of 20–25 Bunsen burners, each of which is provided with a tap and a perforated collar for regulating the supply of air. The flames strike the under side of a semicircular fireclay or sheet-iron trough or gutter in which the combustion tube rests on a layer of magnesia or asbestos. Inclined at an angle over this gutter on either side is a row of fireclay tiles

by which the flame is reverberated upon the upper part of the glass tube, which is thus heated all round. Each tile can be pulled back and rested against an iron rail which runs down each side of the furnace, and thus any part of the tube can be readily examined, and moreover the tiles can be made to assist in regulating the temperature.

In Hofmann's furnace the tube is heated by two double rows of perforated cylindrical fireclay burners placed over ordinary fish-tail burners. The tube rests upon the top of a central row of much shorter burners. The burners are inclosed by flat vertical tiles, and flat tiles are laid horizontally on the top.

In the Glaser furnace the heat is provided by a row of Bunsen burners. The tube is supported by a series of semicircular perforated iron plates, placed close together. The flames strike the bottom of these plates, and then pass through the perforations and strike against the fireclay covers, by which they are reverberated on the tube, so that the latter is heated from the top and sides as well as from the bottom. The tube is usually wrapped round with wire gauze. This furnace will give higher temperatures than the Erlenmeyer furnace, but consumes more gas.

A more modern type of combustion furnace which gives very high temperatures with a small consumption of gas has been introduced by Fletcher. The furnace itself consists of six separate hollow fireclay blocks 6 inches in length and of the same height, which are placed end to end, so as to give a total length of 3 feet. The combustion tube is supported on a fireclay trough placed along the top of the row of furnace blocks which are each pierced along one side with five holes leading to a hollow space immediately below the trough. The main gas-supply pipe is a brass tube of square section which is raised about 1½ inch above the stone
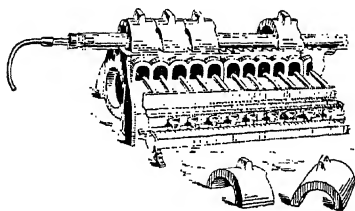
FIG. 16.

bench by terminal brass supports; it carries thirty burners projecting at right angles from it in a slanting direction, so that their nozzles reach upwards to the perforations in the furnace blocks, the centres of these holes being about 3½ inches above the bench. Each furnace block is therefore heated by five burners, and reverberation is ensured by small semicircular fireclay arches, three of which fit loosely on each of the furnace blocks. Owing to their oblique position, the burners are readily kept clean, the brass heating arrangement is quite separate from the earthenware furnace, and the taps and lower parts of the burners are protected from the heat of the furnace by a brass shield running along the whole length of the main gas pipe.

The furnace can be built up in shorter lengths by using fewer of the furnace blocks, of which two are represented in Fig. 16.

To avoid the necessity for using an india-rubber stopper between the combustion tube and the water-absorption apparatus, Marek suggests a mercury joint made by drawing out the combustion tube to a conical end, and fixing round this a knee tube by means of asbestos and fused silver chloride. The knee joint, which is loosely filled with silver ribbon, fits into a bell-shaped tube dipping under mercury (J. pr. Chem. 1907, [2] 76, 180).

The combustion tube should consist of infusible potash or Bohemian glass 1·5–2 mm. thick, with an internal diameter of 12–15 mm. It should be of such a length that it projects about 2 cm. from each end of the gutter or trough. Pieces of copper wire gauze about 2 cm. broad, heated in a flame to remove grease, are rolled up into plugs which fit moderately tightly in the tube, and one of these plugs is pushed into the tube to a distance of about 25 cm. from one end. The tube is then filled with freshly ignited granular cupric oxide to within 5 or 6 cm. of the other end, and a second plug is inserted. The granules of cupric oxide should be fairly regular in size, and 1·5–2 mm. cube. Another plug about 10 cm. long is made by rolling a piece of copper gauze round a stout copper wire 12 cm. long, and bending the projecting end of the latter into a loop by means of which it can be withdrawn from the tube. This plug is placed in the other end of the tube behind the boat. The end of the tube nearest to the copper oxide is fitted with a dry caoutchouc stopper perforated to receive the tube of the absorption apparatus; the other end is closed by a similar stopper, which carries a piece of tubing of very narrow bore, which is connected with the apparatus for drying the oxygen.

The substance to be analysed is contained in a platinum or porcelain boat about 70 mm. long and 8 mm. deep, of such diameter that it slides easily in the combustion tube. It may conveniently be inclosed in a small well-corked tube while being weighed.

The water is absorbed by granulated anhydrous calcium chloride, which is treated with a
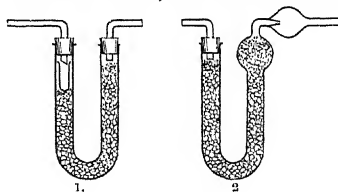
FIG. 17.

current of dry carbon dioxide, and then with a current of dry air to convert any calcium oxide present into carbonate, and thus prevent the absorption of carbonic dioxide.

The calcium chloride is contained in a U-tube provided with a small side bulb for condensing the water, the tube from this bulb fitting directly into the cork in the combustion tube, whilst the other limb of the U-tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle and connected with the potash bulbs (Figs. 18

and 19). In the absence of the side bulb, each limb of the tube is closed by a caoutchouc cork carrying a narrow tube bent at a right angle, one of these tubes fitting directly into the cork of the combustion tube, and the other being connected with the potash bulbs. A small test-tube, 2–3 cm. long, placed in the upper part of the first limb of the ∪-tube, collects the greater part of the water, and thus protects the calcium chloride (No. 1, Fig. 17). (For other forms of calcium chloride tubes, v. Chem. Soc. Proc. 1906, 22, 87; Chem. Zeit. 1907, 31, 342.)

A ∪-tube containing pumice moistened with strong sulphuric acid may also be used to collect the water, but bulbs filled with the acid must not be used, since it dissolves an appreciable quantity of carbon dioxide.

The carbon dioxide is absorbed in a strong solution of potassium hydroxide made by dis-
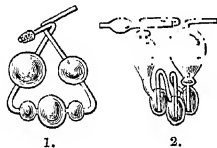
Fig. 18.

solving this substance in an equal quantity of water. The solution is contained in 'potash bulbs,' of which there are many forms. Geissler's form is the most convenient, since it will stand on its own base (No. 2, Fig. 18). Liebig's original form (No. 1) is still used, but the more recent
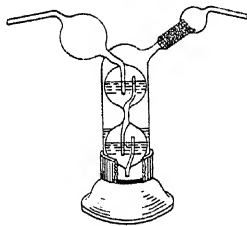
Fig. 19.

form devised by Bender (Fig. 19) secures efficient absorption, and is convenient for weighing, as it stands either on its own base or on an aluminium foot.

The Geissler or Liebig bulbs must contain such a quantity of caustic potash solution that it washes up to a certain extent in the last bulb, but yet is not sufficient to fill the large first bulb in case a vacuum is produced by rapid absorption of the gas. In addition to the potash bulbs, a ∪-tube filled with granulated soda-lime, with a layer of calcium chloride 2 cm. deep in the upper part of each limb, is used to absorb the last traces of the gas and any small quantity of moisture that may be given off from the caustic potash solution. Two such soda-lime tubes may be used in place of potash bulbs. (For other forms of carbon dioxide absorption tubes, v. Chem. Zeit. 1905, 29, 569; 1907, 31, 342; 1908, 32, 77; Amer. Chem. J. 1906, 35, 309; Ann. Chim. anal. 1907, 12, 318; Chem. Soc. Proc. 1908, 24, 182.)

The tube containing the soda-lime is connected with a ∪-tube filled with calcium chloride, to protect the absorption apparatus from moisture; this is especially needful when the air is drawn through the apparatus by means of an aspirator.

The oxygen or air used in the combustion is freed from carbon dioxide by passing through a strong solution of caustic potash. If compressed oxygen is employed, it is advisable to pass it first through a short length of heated combustion tube containing cupric oxide, in order to burn out any carbonaceous impurity. The air or oxygen is then dried by passing through dry calcium chloride or through pumice moistened with concentrated sulphuric acid, the same desiccating agent must be used to dry the gas as is employed to collect the water produced during the combustion.

The oxygen is dried by passing it through two long ∪-tubes containing calcium chloride. Instead of the ∪-tubes we may use a tall cylinder with the lower half filled with soda-lime and the upper with calcium chloride.

The oxygen required for combustions in the open tube may be prepared from potassium chlorate and manganese dioxide and stored over water in gasholders of moderate capacity. The gas may also be generated as required by the following method, which furnishes the gas under sufficient pressure for use in combustions. A solution of 25 grams of potassium permanganate in 500 c.c. of water, and 50 c.c. of sulphuric acid is introduced drop by drop into a litre flask containing 500 c.c. of hydrogen peroxide (10 vols.). The gas contains chlorine and ozone, which are removed during its passage through the purifiers (Bull. Soc. Chim. 1907, [4] 1, 501).

The operation.—The tube is placed in the furnace and connected at one end with the drying apparatus and at the other with the calcium chloride guard tube, but not with the absorption apparatus. It is gradually heated to redness, a current of dry oxygen is passed through for half an hour to remove all moisture and organic matter, and the tube is allowed to cool. When a combustion tube is being used for the first time or after a long interval, it is advisable to carry out a blank experiment by putting on the absorption apparatus and heating the tube for some time in a stream of dry oxygen. If the tube is ready for the analysis, the weight of the absorption tube and apparatus should be constant. The solid or non-volatile liquid substance is now weighed into the platinum boat, which is introduced into the tube by removing the long copper plug at the back, and the latter is then replaced. The front end of the tube is then connected with the absorption apparatus, and the other end is connected with the drying tubes and the oxygen reservoir. The burners under the front part of the tube are now lighted and the temperature gradually raised until the tube is at a dull-red heat to within 12 cm. of the boat. The tube in contact with the stopper at the front end should be so hot that it can only just be touched by the finger, and this temperature should be maintained throughout the operation by regulating the first two burners, in order to prevent condensation of moisture without decomposing the stopper. If any water should condense, it may be volatilised by bringing

one of the hot tiles close over the tube. The last two or three burners under the long copper plug at the back are now lighted and the temperature gradually raised to dull redness, whilst at the same time the copper oxide is heated to within 5–6 cm. of the boat, and a current of oxygen is passed through the tube at the rate of a bubble every two seconds. One of the burners under the boat is then lighted and the boat very gradually heated, combustion being regulated so that the bubbles passing into the potash bulbs can easily be counted. When the substance is completely carbonised, the temperature of the boat is raised and the current of oxygen increased to a bubble per second. Towards the close of the operation the boat is heated to redness and a somewhat more rapid current of gas is passed. It is not necessary to heat the tube above redness, and a higher temperature produces distortion. When combustion is complete, the current of oxygen is continued for a short time to drive out all carbon dioxide and reoxidise any reduced copper. When the oxygen bubbles through the potash bulbs at the same rate as through the drying apparatus, the oxygen reservoir is disconnected and a current of air is drawn through the whole apparatus to expel the oxygen. At the same time the tube is gradually cooled and is ready for a second operation. If the tube is carefully heated and cooled, it may be used for a very large number of analyses. The absorption apparatus is disconnected and weighed. All the weighings should be made without the plugs of caoutchouc tubing and glass rod which are used to protect the contents of the tubes and bulbs from the air. When several analyses are being made of substances which burn only with difficulty, the entire heating may with advantage be carried out in a current of oxygen, and some saving of time is effected by weighing the absorption apparatus filled with oxygen.

Volatile liquids are inclosed in a small thin cylindrical glass bulb 3 cm. long, with a capillary neck, readily made by drawing out a piece of wider tubing. The bulb is weighed, heated, and the capillary tube immersed beneath the liquid. As the tube cools a small quantity of the liquid enters. This is heated to boiling, and when the air is expelled the end of the tube is again placed in the liquid, and when the vapour condenses the bulb is completely filled. If the liquid is very volatile, the capillary end may be sealed before weighing the tube, but usually this is not necessary. The bulb is placed in the boat with the capillary end open and directed towards the copper oxide. Combustion is conducted as already described, but much greater care is required, especially if the liquid is very volatile. The front part of the copper oxide must be quite red-hot before the liquid begins to volatilise, and it is advisable that the bulb be empty before the copper oxide near the boat is heated. With an iron gutter sufficient heat is conducted to vapourise volatile liquids, but in other cases a very low flame may be used, or one of the hot tiles may be held over the boat. In all cases it is difficult to prevent diffusion of vapour into the back of the tube and even into the drying apparatus. The long copper plug at the back increases the speed of the current by decreasing the diameter of the

passage, and the narrow diameter of the entrance tube assists in a similar manner, but in all cases of the analysis of a volatile substance a slow current of air should be passed almost from the beginning. Later, oxygen should be passed, but not too soon, otherwise an explosive mixture may be formed. The open tube, in fact, does not yield such satisfactory results with volatile liquids as with other substances, and in such cases combustion should be made by the following method.

Liebig's original method as modified by Bunsen. Granular cupric oxide and some of the finely divided oxide are heated strongly, and while still hot are placed in flasks with long necks
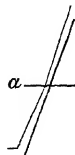
FIG. 20.

which are then tightly corked. The combustion tube is drawn out at one end in the manner shown in the figure, and sealed at the point a. A layer of granular cupric oxide about 10 cm. long is first introduced by placing the combustion tube in the neck of the flask (Fig. 21) containing it, and then 2–3 cm. of the finely divided oxide. The substance (about 0·5 gram) is now introduced from a long narrow weighing tube which can be inserted into the mouth of the combustion tube, and 5–6 cm. of the finely divided oxide is added and intimately mixed with the substance by means of a long copper wire, the lower end of which has two twists like a corkscrew (Fig. 22). The wire and sides of the tube are rinsed with some of the oxide, and the tube is filled with the granular oxide to within 5–6 cm. of the top, and a plug of cupric gauze inserted. Every care must be taken to prevent absorption of moisture by the cupric

FIG. 21.

FIG. 22.

oxide. The remainder of the operation is conducted as described above, and when combustion is complete the drawn-out end of the tube is connected with a drying apparatus, the tip broken off inside the caoutchouc tube, and a current of oxygen and afterwards of air passed through the apparatus.

In whichever way the combustion is made it is found that the percentage of hydrogen is always about 0·1–0·15 too high, a result attributed to the difficulty of perfectly drying the cupric oxide, &c. It is frequently stated that an open tube rarely gives correct results the first time it is used ; but this is solely due to neglect of the precaution of first heating in a current of oxygen (p. 219).

Combustion with lead chromate. Substances such as graphite, resins, &c. which are oxidised with great difficulty, should be burnt with lead chromate, or in extreme cases with lead chromate containing 10 p.c. of potassium bichromate; these oxidising agents can be employed in either open or closed combustion tubes. The chromate is precipitated by adding potassium bichromate to a solution of lead nitrate, washed, dried, fused, and then granulated. It is heated immediately before being used, and the tube is filled in the same manner as with copper oxide in B. The efficiency of the lead chromate depends mainly on the fact that at a high temperature it fuses. After being used it is heated with nitric acid in order to remove the reduced oxides, and is washed, dried, and again ignited.

Carbon and hydrogen in presence of nitrogen, halogens, &c. When nitrogen is present it is partly converted into nitrogen oxides, which are absorbed by the caustic potash. In order to avoid this source of error, the front of the tube contains plugs of copper wire gauze or a layer of granulated metallic copper 12–15 cm. in length reduced in carbonic oxide. The copper is heated to redness throughout the operation, and the nitrogen oxides are decomposed with absorption of oxygen and liberation of nitrogen. A silver gauze plug is preferable to the copper, because if the latter is reduced in hydrogen, it is apt to retain water, and if in methyl alcohol, it may also contain carbon (Zeitsch. anal. Chem. 1906, 14, 741).

Perkin (Chem. Soc. Proc. 1880, 37, 457) employs precipitated manganic oxide made into a paste with a saturated solution of potassium chromate containing 10 p.c. of dichromate, dried and granulated. A layer of this mixture 15 cm. long is placed in the front of the tube and heated to 200°–250° C. All nitrogen oxides are absorbed, but if the mixture is heated too strongly they are partially expelled. After each analysis the manganic oxide is heated more strongly whilst a current of air is passed through the tube, and the nitrogen oxides are more or less completely driven off.

The halogens, when present, form halide copper salts, which are somewhat volatile and are liable to be carried into the absorption apparatus. In such cases the front layer of copper may be replaced by silver foil or gauze, which decomposes the nitrogen oxides and also absorbs the halogens. Compounds of this kind may also be burnt by means of lead chromate, (*v. supra*), or a mixture of the substance with lead chromate may be placed in a porcelain boat and burnt in a current of oxygen in the usual way (*cf.* Amer. Chem. J. 1906, 35, 531).

Sulphur forms sulphur dioxide, which is absorbed by caustic potash. Compounds containing this element may be burnt with lead chromate, care being taken that the front of the tube is not too hot; or the front of the tube may contain a somewhat longer layer of manganic oxide and potassium chromate, the front half being kept at 200°–250° to absorb nitrogen oxides, whilst the rear half is heated to dull redness and absorbs the sulphur dioxide (Perkin, *l.c.*).

Combustion in presence of a contact substance. The use of a special combustion furnace may be obviated by bringing a mixture of oxygen and the vapour of the organic substance heated to a suitable temperature, into contact with some active material, such as platinum, platinised quartz, platinised asbestos, palladium, or even finely divided copper oxide. This process, which has been applied successfully by Dennstedt and his collaborators to a varied series of organic substances, is carried out in a hard-glass or quartz combustion tube, about 86 cm. in length and 16–18 mm. in diameter, the contact material being placed about the middle of the tube. Platinised quartz is prepared by soaking thoroughly clean and dry quartz fragments in an alcoholic solution of pyridine platinichloride and igniting them over the blow-pipe. A layer of about 3 cm. of this material can be used in the combustion, or platinum foil or wire may be employed, one of the most efficient forms of this metal being a six-rayed star of platinum foil, about 10 cm. in length. The combustion is most conveniently effected in a double supply of oxygen. The boat containing the substance is placed in the hard-glass inner tube (18 cm. in length) shown in Fig. 23, which is open at one end and at the
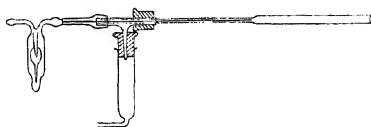
other terminated by a wide capillary tube, through which a current of dry oxygen can be introduced. This inner tube has a diameter of about 14 mm., and oxygen can be passed through the annular space by means of the T-tube fitting over the capillary tube as shown in the figure.

By means of this apparatus the supply of oxygen required for vaporising and burning the substance can be carefully regulated. When the organic compound contains nitrogen, sulphur, or halogens, a large boat containing lead peroxide is placed in the combustion tube and heated to 300°–320°. The sulphur is absorbed in the form of lead sulphate, and may be estimated by extracting the lead peroxide with 5 p.c. sodium carbonate solution, and estimating the sulphate in the filtrate. The estimation of chlorine and bromine may be similarly effected. Iodine is not entirely absorbed by lead peroxide, and, accordingly, 'molecular' silver must be employed to take up this element (Dennstedt, Zeitsch. angew. Chem. 1905, 18, 1134; 19, 517; Chem. Zeit. 1905, 29, 52; 1909, 33, 769; Analyst, 1905, 135; Ber. 1908, 41, 600; Baumert, Ber. 1907, 40, 3475). Walker and Blackadder recommend a furnace 60 cm. long, with granular copper oxide partly placed in the combustion tube and partly mixed with the weighed substance. The combustion is carried out in about 30 minutes, and the tube can be heated with Bunsen burners on an ordinary working bench (Chem. News, 1909, 99, 4; *cf.* Marek J. pr. Chem. 1906, 73, 359).

Electrical method. In this process the electric current is used as the source of heat, and platinum as the catalyst. A Dennstedt inner

tube is employed to contain the boat z with the weighed substance, and the spiral of platinum-iridium wire NJ is wound round a porcelain or quartz tube held in position in the combustion tube by a nickel tube DE, passing through the indiarubber stopper C. The coil is heated to redness by the passage of the current through DKJOP, and the absorption apparatus is fitted on to the outer end of the nickel tube DE. A divided stream of oxygen is employed as in the Dennstedt process, and the time required for complete combustion varies from 15 to 40 minutes.

The consumption of electrical energy in
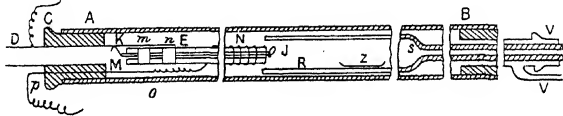
FIG. 24.

this method of carrying out combustions is small, amounting to about 3·6 amperes at 54 volts (194·4 watts) during the time when the highest temperature is obtained (Breteau and Lerona, Bull. Soc. chim. 1908, [4] 3, 15; *cf.* B. Blount, Analyst, 1905, 30, 29; Morse and Taylor, Amer. Chem. J. 1905, 33, 591; Morse and Gray, Amer. Chem. J. 1906, 35, 451; Carrasco and Plancher, Gazz. chim. ital. 1906, 36, 492; Lippmann, Chem. Zeit. 1905, 29, 487, 174; Tucker, J. Amer. Chem. Soc. 1907, 29, 1442).

Nitrogen. This element is determined in the form of ammonia (Will and Varrentrapp, Ruffle, Kjeldahl), or in the form of nitrogen gas, which is collected and measured, the weight being calculated from the volume (Dumas, Maxwell Simpson).

A. *Will and Varrentrapp's method.* The substance is heated with soda-lime and the nitrogen is evolved as ammonia, which is absorbed in hydrochloric acid and precipitated as ammonium platinichloride or estimated volumetrically. This method is not applicable to azo-, diazo-, nitro-, and nitroso- derivatives, and to certain albuminoid substances.

Soda-lime is prepared by slaking 2 parts of good quicklime with a strong solution of 1 part of sodium hydroxide free from nitrates or sulphates. The mixture is dried by heating in an iron vessel, granulated, and preserved in well-closed bottles. A mixture of equal parts of calcium hydroxide and anhydrous sodium carbonate may also be used.

A glass tube about 50 cm. long and 12 mm. diameter, sealed at one end, is filled to a depth of about 5 cm. with a mixture of anhydrous oxalic acid and granular soda-lime, and a short plug of recently ignited asbestos is inserted. The substance is intimately mixed with sufficient finely powdered soda-lime to form a layer about 15 cm. long, and is quickly introduced into the tube. The mortar is rinsed with a small quantity of soda-lime, which is also put in the tube, and the latter is then filled with granular soda-lime to within 5 cm. from the end and a loose asbestos plug inserted. The tube is tapped to form a channel over the powdered soda-lime for the escape of the gases, and is placed in a furnace, which may be considerably shorter than that used in the estimation of hydrogen and oxygen. The combustion tube is attached by means of a perforated cork to an apparatus for absorbing the ammonia. This may consist of the bulbs originally devised by Will and Var-

rentrapp, or of an ordinary bulb U-tube. Winkler has devised a combination of bulb and flask which is especially convenient for estimations by titration, since the liquid need not be transferred. Ordinary dilute hydrochloric acid or a definite volume of standard acid is placed in the bulb. The tube is gradually heated to redness, beginning at the end near the U-tube, and when decomposition is complete the oxalic acid at the back is heated, and the ammonia in the tube is driven out by the current of carbonic oxide and carbon dioxide. The excess of acid is then determined by standard alkali; or the liquid is evaporated with platinic chloride as in an ordinary estimation of ammonia, and the precipitate is washed with ether containing a small quantity of alcohol, dried, heated in a crucible till completely decomposed, and the nitrogen calculated from the weight of the residual platinum. $Pt = N_4$. The nitrogen frequently forms volatile bases other than ammonia, and hence the platinum precipitate cannot be weighed as such. The ratio of platinum to nitrogen is, however, the same in all cases. The precipitate is washed with ether, because if such bases are present, it may be soluble in alcohol.

It is important that the front part of the tube be heated sufficiently to secure complete decomposition, but the temperature must not be too high, otherwise part of the ammonia itself is decomposed, and the results are too low. Substances rich in nitrogen should be mixed with some pure sugar in order to dilute the ammonia and prevent too rapid absorption.

Various modifications of Will and Varrentrapp's method have been introduced in order to make it more generally applicable, but these processes have been superseded by Kjeldahl's method (*cf.* Ruffle, Chem. Soc. Trans. 1881, 39 87; Arnold, Ber. 1885, 18, 806).

B. *Dumas' method.* In this process the hydrogen and carbon are burnt by means of cupric oxide and the liberated nitrogen collected and measured. A glass tube 80 cm. long, 12 to 15 mm. diameter, sealed like a test-tube at one end, is filled to a length of 12–15 cm. with dry sodium hydrogen carbonate, 4 cm. of cupric oxide is added, and then an intimate mixture of the substance (0·3–0·6 gram) with cupric oxide, then the cupric oxide used to clean the mortar, a layer of granular cupric oxide, and finally a layer of reduced granulated copper or copper-wire gauze not less than 15 cm. in length. The tube is connected by means of a cork and

bent tube with an apparatus for collecting the nitrogen. The sodium hydrogen carbonate is first heated until all air is expelled and the issuing gas is completely absorbed by potash solution. The copper is then heated to redness, the heat being gradually applied to the whole tube as far as the carbonate. When combustion has ceased, the carbonate is again heated until all the nitrogen has been expelled.

The most convenient form of apparatus for collecting the nitrogen is that devised by H. Schiff (Zeitsch. anal. Chem. 7, 430), or a similar form described by Groves (Chem. Soc. Trans. 1880, 37, 500). The former consists of a burette, A, fitted with a heavy foot and provided with a stop-cock, c, at the top. Close to the bottom is a tubulus, b, inclined at an angle of about 45°, and on the other side is another tubulus, a, connected by means of a caoutchouc tube previously soaked in paraffin with a globular reservoir, B, which is attached to the burette by a clip, and the height of which is readily adjusted. Mercury is poured into the burette through the lower tubulus to a height of 2 or 3 mm. above the lower opening, and the reservoir is then filled with a solution of caustic pot-

FIG. 25.

ash in its own weight of water, the lower tubulus being closed with a cork. The stop-cock is opened and the reservoir raised until the burette is completely filled with the alkaline solution. The stopcock is then closed and the reservoir lowered to the bottom of the burette. The tubulus may now be opened without the mercury or alkaline solution being forced out. When the air has been expelled from the combustion tube the end of the delivery tube is inserted through the tubulus and the nitrogen collected. At the close of the operation the temperature of the gas is allowed to become constant, the reservoir is raised so that the level of the liquid is the same as in the burette, and the volume of the nitrogen is read off, together with the temperature and the height of the barometer. The weight of the nitrogen, P, is then calculated from the volume by means of the formula

$$P = \frac{V(B - f)0 \cdot 001251}{(1 + 0 \cdot 00366t)760},$$

where V is the observed volume, B the height of the barometer, f the tension of aqueous vapour at the temperature t, and $0 \cdot 001251$ the weight of 1 c.c. of nitrogen at 0° and 760 mm.

Gatterman (Zeitsch. anal. Chem. 24, 57) collects the nitrogen in an apparatus similar to Schiff's, but not graduated. A bent tube of small diameter completely filled with water is attached to the jet of the burette by means of caoutchouc tubing. By closing the lower tubulus, raising the potash reservoir, and opening the stopcock, the gas is driven over into a graduated tube standing over water, and is measured. The error due to the unknown vapour tension of the potash solution is thus avoided, but the vapour tension of the water at the particular temperature must of course be taken into account. Other forms of apparatus are described by Zulkowsky (Annalen, 1876, 182, 296; Roscoe and Schorlemmer's Chemistry, 3, pt. 1, 74) and Schwarz (Ber. 1880, 13, 771).

C. *Maxwell Simpson's modification of Dumas' method* (Chem. Soc. Trans. 1853, 6, 290; Annalen, 1855, 95, 74). In order to avoid the formation of carbonic oxide and nitric oxide, the substance is burnt with a mixture of cupric oxide and mercuric oxide. Into a tube similar to that used in Dumas' method is introduced about 12 grams of manganese carbonate or granulated magnesite mixed with 2 grams of precipitated mercuric oxide, followed by a plug of asbestos. Another gram of mercuric oxide is introduced, and then an intimate mixture of $0 \cdot 5$ gram of the substance with 45 parts of a previously prepared and thoroughly dry mixture of 4 parts of ignited cupric oxide and 5 parts of precipitated mercuric oxide. The mortar and the sides of the tube are rinsed with a similar mixture and another asbestos plug is introduced. A layer of granular cupric oxide about 9 cm. in length and a layer of not less than 20 cm. granulated copper, kept in position by another asbestos plug, fill the remainder of the tube. After the air has been expelled by heating the manganese carbonate or magnesite, the tube is gradually heated to redness, beginning from the front. The metallic copper not only decomposes nitrogen oxides, but also absorbs the excess of oxygen. The gas is collected as in Dumas' method, the magnesite or manganese carbonate providing the carbon dioxide.

Certain organic compounds (*e.g.* hydroaromatic series), when analysed for nitrogen, evolve a portion of their carbon as methane, which, being burnt only imperfectly, adds to the volume of the nitrogen. In these cases lead chromate is recommended as the oxidising agent, or the substance may be mixed with cuprous chloride and copper oxide (Haas, Chem. Soc. Proc. 1906, 22, 81).

Various modifications of Dumas' process have been proposed. Thudichum and Wanklyn use a mixture 5 parts of normal sodium carbonate and 13 parts of fused potassium bichromate in place of sodium hydrogen carbonate. Groves (*l.c.*), with a view to using the same tube repeatedly, places the mixture of carbonate and bichromate in a small tube connected with the combustion tube by an indiarubber joint. The portion of the cupric oxide mixed with the substance is separated from the layer remaining always in the tube by means of a tight plug of asbestos and copper gauze, the latter keeping a free passage for the gas.

The combustion tube may be open at both ends, the rear being connected with an apparatus for generating carbon dioxide, but special precautions must be taken to obtain this gas free from air (*v.* Warington, Chem. Soc. Trans. 1882, 41, 346).
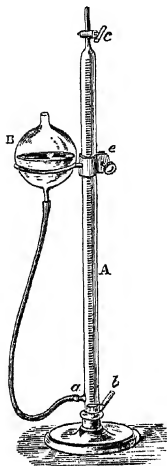
The carbon dioxide required for this modification of Dumas' process may be generated in a Kipp's apparatus by the action of hydrochloric acid on marble or calcite. These minerals should, however, be boiled with water before being used, in order to free them from air. The dioxide may also be generated by dropping a concentrated solution of potassium carbonate (sp.gr. 1·5) into a mixture of water and concentrated sulphuric acid. A convenient apparatus in which to effect this operation is shown in the accompanying figure (Young and Caud-
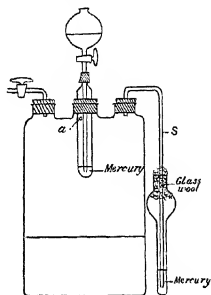
Fig. 26.

well, J. Soc. Chem. Ind. 1907, 26, 184). The carbonate solution flows from the dropping funnel into the mercury trap and out into the Woulff's bottle through the small hole a. The rate of evolution is regulated by the exit tap, and s is a safety tube.

In both Dumas' method and Simpson's modification the combustion tube may be drawn out at the front end and connected with a Sprengel mercury pump by glass tubing joined by short pieces of caoutchouc tubing, the joints being surrounded by short wide tubes filled with water or glycerol. A bulb is blown on the
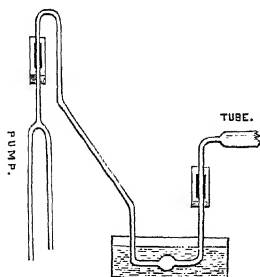
Fig. 27.

horizontal part of the glass tube at the end near the combustion tube, and this bulb is kept cool during the operation, and serves to condense the water which is formed. The combustion tube is made vacuous, and when no more air issues from the end of the pump, the combustion is conducted in the ordinary way, the gas which is evolved being pumped out by the Sprengel pump and collected in a suitable tube. No magnesite

need be used. The copper oxide keeps the exhausted tube from collapsing when heated.

In many cases, especially with nitro- derivatives, the gas generated in the exhausted tube is a mixture of nitrogen with nitric oxide, the latter being sometimes present in considerable quantity. It is advisable, therefore, to decompose the nitric oxide by using either a layer of reduced copper or a long plug of silver gauze placed between the copper oxide and the exit, and by keeping this material heated throughout the combustion.

Liquids in which nitrogen is to be determined may be enclosed in bulbs which are dropped into the combustion tubes as in the determination of hydrogen and oxygen.

The copper oxide used in nitrogen determinations should be prepared by heating metallic copper in air and never by ignition of the nitrate, since in the latter case it is apt to contain basic nitrates which evolve nitrogen on heating.

The copper used in nitrogen determinations, &c., should not be reduced in hydrogen, since it is liable to occlude this gas. It may be reduced in the mixture of carbon monoxide and carbon dioxide obtained by heating oxalic acid with strong sulphuric acid. Plugs of copper gauze may also be reduced by heating them to redness and dropping them into a test-tube containing a few drops of formic acid or methyl alcohol. The reduced copper is carefully dried at 100°–110°.

When no carbonate is used and the gas is simply pumped out of the tube and collected over mercury, it consists of a mixture of carbon dioxide and nitrogen. If the former is estimated by absorption with caustic potash, a determination of the carbon may be combined with that of nitrogen.

Jannasch and Meyer have described a method for the simultaneous estimation of carbon, hydrogen, and nitrogen (Ber. 1886, 19, 949 ; Annalen, 1886, 233, 375 ; Zeitsch. anal. Chem. 1887, 26, 86 ; cf. Bull. Soc. chim. 1905, 33, 951).

D. Kjeldahl's method (Zeitsch. anal. Chem. 1883, 22, 366). The substance is heated with concentrated sulphuric acid to a temperature approaching the boiling-point of the latter, and when decomposition is complete, an excess of solid potassium permanganate is added. The nitrogen is thus converted into ammonium sulphate, which is then distilled with excess of alkali and the ammonia collected and estimated. This method is economical, requires no combustion furnace or special apparatus, is rapid, and requires comparatively little attention, so that a large number of determinations can be carried on at the same time. The substance need not be in a very fine state of division, and the method is especially suitable for liquid and pasty substances such as extracts.

It is important that the sulphuric acid employed for these determinations should be protected from ammonia, and the caustic soda solution should be well boiled in order to expel any ammonia which it may contain. The purity of the reagents is best ascertained by making an experiment with pure sugar. If a small quantity of ammonia is present, the same quantity of the reagents should be used in each experiment, and a correction made for the ammonia which they contain.

In order to prevent bumping during distillation,

a small piece of zinc may be placed in the flask, but it is essential that the soda should be free from nitrates and nitrites, which would be reduced and yield ammonia.

The time required for the operation may be considerably shortened by using sulphuric acid containing sulphuric anhydride or phosphoric anhydride.

The method as thus carried out is applicable to all substances which can be analysed by Will and Varrentrapp's process, and to many others.

Heffter, Hollrung, and Morgen (Zeitsch. f. Chem. 8, 432) treat 1·0–1·5 grams of substance with 20 c.c. of a mixture of 4 vols. ordinary sulphuric acid and 1 vol. of fuming acid, and 2 grams of phosphorus pentoxide. Kreusler (Zeitsch. anal. Chem. 1885, 24, 453) uses sulphuric acid containing 200 grams of phosphorus pentoxide per litre.

Wilfarth (Chem. Zentr. [3] 16, 17, 113) finds that the oxidation of the organic matter takes place much more rapidly in presence of certain metallic oxides. Mercuric oxide is the most efficient, but cupric oxide answers almost equally well. The former produces mercuriammonium derivatives, which are not readily decomposed by caustic soda, and hence the alkaline liquid must be mixed with some potassium sulphide to decompose the mercury compounds. The mercuric sulphide formed makes the liquid boil regularly without the addition of zinc. Ulsch recommends the use of ferrous sulphate instead of potassium sulphide; it may be added before the caustic soda.

Warington (Chem. News, 1885, 52, 162) removes nitrites and nitrates by boiling with ferrous sulphate and hydrochloric acid.

With a view to secure the reduction of nitroderivatives, &c., and thus make the process generally applicable, Asboth (Chem. Zentr. [3] 17, 161) mixes 0·5 gram of the substance with 1 gram of pure sugar in the case of readily oxidisable compounds, and with 2 grams of benzoic acid in the case of nitrates and similar derivatives. Most probably the benzoic acid first forms nitro- derivatives, which are afterwards reduced. He adds Rochelle salt with the caustic soda in order to prevent precipitation of manganese, &c., and thus avoids bumping during distillation. With these modifications the method is applicable to all nitrogen compounds except those of the pyridine and quinoline series. E. Arnold (ib. p. 337) uses 0·5 gram of anhydrous cupric sulphate and 1 gram of metallic mercury in place of the oxides as recommended by Wilfarth, and heats 1 gram of the substance with these and 20 c.c of sulphuric acid containing 20–25 p.c. of phosphoric oxide.

C. Arnold (Arch. Pharm. [3] 24, 785) confirms Asboth's statements, but finds that in addition to pyridine and quinoline compounds, azo- derivatives and nitrites yield unsatisfactory results. He heats 0·5 gram of substance with 0·5 gram of anhydrous cupric sulphate, 1 gram of metallic mercury, 2 grams of phosphoric oxide, 1 gram of sugar, and in case of nitrates, &c., 2 grams of benzoic acid, and 20 c.c. of sulphuric acid.

Reitmair and Stutzer (Rep. Anal. Chem. 5, 232; Zeitsch. anal. Chem. 1886, 25, 582) use about 0·7 gram of mercuric oxide and 20 c.c of sulphuric acid, with a small fragment of paraffin

n the case of substances rich in fat. They regard the use of phosphoric oxide as unnecessary, and the use of fuming sulphuric acid as undesirable on account of its liability to contain nitrogen oxides.

Jodlbauer (Chem. Zentr. [3] 17, 433) uses phenolsulphonic acid in place of benzoic acid, and reduces with zinc dust. He thus obtains good results even with nitrates. Reitmair and Stutzer (Rep. Anal. Chem. 7, 4) find that the nitrate must be somewhat finely divided; 0·5 to 1·0 gram of the substance is mixed with 50 c.c. of sulphuric acid containing 20 grams of phenol per litre, allowed to stand for a short time with occasional agitation, mixed with 2–3 grams of dry zinc powder and 1 or 2 drops of metallic mercury, and heated in the usual way. Conversion into ammonium sulphate requires one and a half hours.

A most important improvement in the Kjeldahl process due to Gunning (Zeitsch. anal. Chem. 28, 188), consists in the addition of potassium sulphate to the concentrated sulphuric acid. The solution of potassium hydrogen sulphate in concentrated sulphuric acid boils at a temperature considerably above the boiling-point of the strong acid and the oxidation of the organic matter is thereby greatly facilitated. Various oxidising and catalytic agents may be employed in conjunction with this mixture, and the following are among the many which have been suggested in addition to those already mentioned: platinic chloride, ferric chloride, manganese dioxide, magnesia, and sodium phosphate. The use of potassium permanganate has now been abandoned, and, in the case of refractory substances, oxidation is now generally induced by the catalytic action of mercury or its oxide. The following process is described by Dyer (Chem. Soc. Trans. 1895, 67, 811). The substance (0·5–5 grams) is introduced into a roundbottomed Jena flask, and heated gently with 20 c.c. of concentrated sulphuric acid containing a small globule of mercury. After the initial action has subsided, the temperature is raised to boiling, and in 15 minutes 10 grams of potassium sulphate are added, and the boiling continued till the solution is clear and colourless. The flask is closed with a loosely fitting bulb stopper, from the internal projection of which the condensed sulphuric acid drops back into the flask. There is, therefore, little loss of acid except through reduction to sulphurous acid. The product is rinsed into a capacious Jena distilling flask, rendered strongly alkaline with sodium hydroxide, with the addition of a small quantity of sodium sulphide, and the liquid distilled in a current of steam, the ammonia being collected and estimated in the usual way.

When nitrates are present, Jodlbauer's modification is employed, but the phenol may conveniently be replaced by salicylic acid. When the solution of this substance in concentrated sulphuric acid is poured quickly on to the weighed material, the loss due to the formation of lower oxides of nitrogen is avoided, and satisfactory results are obtained even when ammonium nitrate is present. This circumstance is of great importance in connection with the analysis of compound fertilisers containing both ammonium salts and alkali nitrates. The

zinc and mercury are added while the solution is still cold, and the former metal allowed to dissolve before the mixture is heated. Other reducing agents, such as sugar and sodium thiosulphate, may be used either alone or in conjunction with zinc. By the aid of this modified process satisfactory results are obtained in the analysis of organic nitro-,azo-,and hydrazo-derivatives. It has not been found possible to obtain correct estimations of nitrogen in sodium nitroprusside, phenylhydrazine and its deriva-tives, and in mixtures containing large propor-tions of chlorides and nitrates (cf. J. Amer. Chem. Soc. 17, 567; Analyst, 1905, 314; Ber. 1905, 38, 559; Chem. Soc. Proc. 1901, 25, 351; 1903, 27, 988).

The literature of nitrogen determinations is extremely voluminous. Summaries of contribu-tions to this subject will be found in Zeitsch. anal. Chem. 1884, 23, 551; 24, 439; 25, 424 and 571; 26, 249; and Chem. News, 1888, 57, 62, et seq. In addition to the references already given, papers relating to Kjeldahl's process may be found in Zeitsch. anal. Chem. 24, 199, 388, and 393; 25, 149 and 155; 26, 92; 27, 222 and 398.

Chlorine, bromine, and iodine.

By lime. A tube about 40 cm. long and 7 mm. diameter, sealed at one end like a test-tube, is filled to a depth of 5 cm. with pure granulated quicklime. The substance is weighed into the tube and mixed with finely powdered lime by means of a copper wire twisted at the end like a corkscrew. The wire and tube are rinsed with lime, the tube is filled to within 5 cm. of the open end with granulated lime. The tube is gradually heated to redness from the front. When cold the contents of the tube are dissolved in water slightly acidified with nitric acid, filtered, and the halogen precipitated by silver nitrate.

In the case of iodine the substance is dissolved in water, filtered, mixed with silver nitrate, and finally acidified, in order to avoid liberation of iodine. A further precaution consists in adding a little sodium sulphite before each addition of nitric acid.

When the substance contains nitrogen, cyan-ides may be formed; but this is avoided by using pure soda-lime in place of lime. If the lime contains sulphates, some sulphide is liable to be produced. (On the preparation of pure lime, *see* Zeitsch. anal. Chem. 4, 51 and 15, 5.)

Liquids are contained in small bulbs with capillary openings, which are dropped into the tube before filling up with lime. The tube must be very gradually heated, and should be longer than usual.

Carius's method (Annalen, 1860, 116, 1; 1865, 136, 129; Ber. 1870, 3, 697). The substance is oxidised by heating with nitric acid in sealed tubes in presence of silver nitrate. In many cases acid of sp.gr. 1·2 and a temperature of 120°–200° will suffice; but substances which are more difficult to oxidise require acid of sp.gr. 1·42, mixed in special cases with some potassium dichromate, or the fuming acid of sp.gr. 1·5 may be used. If necessary the tubes may be heated as high as 300°. The quantity of acid used should not be more than twice that theoretically required for complete oxida-tion, and the tube must not contain more than

4 grams of nitric acid for each 50 c.c. of its volume. If the operation is prolonged, it is desirable to reduce the pressure in the tube by opening it from time to time by heating the capillary end of the previously cooled tube in a flame until it softens, when the gas forces its way out.

The weighed substance is enclosed in a narrow tube of thin glass of such length that its mouth projects above the nitric acid in the tube, and the acid does not come in contact with the substance until the tube is sealed. The tubes used should be about 15 mm. in diameter and 1·5–2 mm. thick in the glass. After introduction of the substance they are drawn out to a capillary tube with thick walls, which is then sealed. The sealed tubes are heated in a pressure tube furnace tilted at one end so that the capillary ends of the tubes do not come into contact with the liquid. After being heated, the tubes should on no account be removed from the protecting iron or steel tube until they have been opened. For this purpose the tubes are held in position by means of a cork collar through which the capillary ends project out of the furnace. The capillary end is first gently warmed to volatilise any con-densed acid, and then heated more strongly until the gases under pressure blow a hole through the softened tip of the sealed capillary. In this operation the pressure of the imprisoned gases is very great, and it is extremely dangerous to attempt to open the tube with a file. The tube furnace should only be used for this pur-pose within a well-protected enclosure (Fig. 28), so as to minimise the personal risks arising from explosions of the heated tubes.
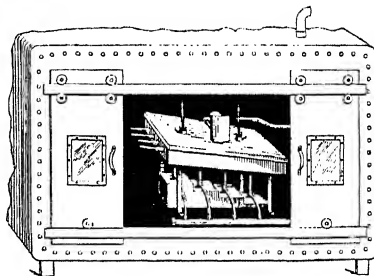
FIG. 28.

The silver salt formed is rinsed out of the opened tube and treated in the usual way.

For the estimation of iodine in organic com-pounds this method is to be preferred to the lime process, but as the silver nitrate and silver iodide frequently form a fused yellow mass, the mixture must be extracted thoroughly with hot water in order to remove the former salt. The silver halide obtained by the Carius method is collected in a tared Gooch crucible, washed successively with water and alcohol, dried at 100°, and weighed.

Stepanow's method. The substance is boiled with alcohol (20–40 c.c.) and sodium is added at such a rate that a vigorous reaction is main-tained. A large excess of the metal is essential

$$XCl + 2Na + C_2H_5 \cdot OH = XH + NaCl + C_2H_5 \cdot ONa.$$

When all the sodium has dissolved, 20–40 c.c. of water are added, and the alcohol removed by distillation. The aqueous solution is acidified with nitric acid, and the halogen estimated gravimetrically, or volumetrically by Volhard's method (Ber. 1906, 39, 4056; cf. Bacon, J. Amer. Chem. Soc. 1909, 31, 49). By using the latter method and weighing the mixed silver halides, the two halogens can be estimated indirectly in the same compound.

Pringsheim's method consists in burning the organic substance with sodium peroxide. Compounds containing more than 75 p.c. of carbon are mixed with 18 parts of this oxidising agent, and those with 50–75 p.c. of carbon with 16 parts. Substances containing less than 25 p.c. of carbon are mixed with sugar or naphthalene, and treated with 16–18 parts of the peroxide. The mixture is placed in a steel crucible surrounded by water and having a perforated lid through which a glowing iron wire is thrust to cause ignition. The product is extracted with water, acidified with nitric acid, and the halogen estimated in the usual way (Ber. 1903, 36, 4244; 1904, 37, 324; 1905, 38, 2459; Amer. Chem. J. 1904, 31, 386; *cf.* Moir, Chem. Soc. Proc. 1907, 23, 233; Baubigny, Bull. Soc. chim. 1908, (iv.) 3, 630).

Sulphur and phosphorus.

Non-volatile substances. Pure caustic potash is fused in a silver dish with about one-sixth its weight of potassium nitrate and a little water. When cold the substance is weighed into the dish, which is again heated, the substance being mixed with the alkali by means of a silver spatula. When oxidation is complete, the mass is allowed to cool, and is then dissolved in water acidified with hydrochloric acid, and the sulphuric or phosphoric acid estimated in the usual way.

Carius's method is carried out exactly as in the estimation of the halogens. Sulphur is oxidised to sulphuric acid and phosphorus to phosphoric acid. It is advisable to remove the greater part of the nitric acid before precipitating barium sulphate or magnesium ammonium phosphate.

Another method applicable to volatile and non-volatile substances is as follows:—Into a combustion tube 40 cm. long, sealed at one end, is introduced 2–3 grams of pure mercuric oxide, then a mixture of the substance with equal proportions of mercuric oxide and pure anhydrous sodium carbonate, and the remainder of the tube is filled with sodium carbonate mixed with a small quantity of mercuric oxide. The open end of the tube is closed by a cork carrying a glass tube dipping under water, in which the mercury is condensed. The tube is carefully heated so that the front layer of sodium carbonate is red hot before the substance begins to volatilise. The substance is then rapidly heated, so that decomposition is complete in about fifteen minutes, and finally the mercuric oxide at the rear end of the tube is heated until oxygen issues from the end of the delivery-tube (Russell, Chem. Soc. Trans. 1854, 7, 212; J. pr. Chem. 1855, 64, 230). The contents of the cooled tube are dissolved in water, a small quantity of bromine water added to oxidise any sulphide, the solution acidified with hydrochloric acid, boiled to expel bromine, and the sulphuric

acid or phosphoric acid estimated in the usual way.

Many non-volatile substances may be oxidised by heating with pure concentrated caustic potash solution, diluting with twice the volume of water, and treating with a current of chlorine. After complete oxidation the solution is acidified, heated to expel chlorine, and the sulphuric or phosphoric acid determined.

Arsenic. The estimation of this element in organic compounds has recently acquired increased importance owing to the application of these substances in therapeutics. One of the earliest methods, due to La Coste and Michaelis (Annalen, 1880, 201, 224), consisted in mixing the substance with soda-lime, and heating the mixture in a stream of air or oxygen. The residue was dissolved in nitric or hydrochloric acid, the arsenic precipitated as sulphide, and afterwards converted into magnesium pyroarsenate. Monthoulé recommends destroying the organic matter with nitric acid containing magnesium nitrate, when a final ignition leads to the formation of magnesium arsenate (Ann. Chim. anal. 1904, 9, 308).

Pringsheim oxidises the organic arsenic derivative with sodium peroxide, and estimates the arsenic as magnesium pyroarsenate (Amer. Chem. J., 1904, 31, 386).

The following procedure has been shown to be applicable to the organic arsenical drugs now on the market. The substance (0·2–0·3 gram) is mixed with 10–15 grams of sodium peroxide and sodium carbonate in equal proportions, the mixture heated gently in a nickel crucible for 15 minutes, and the temperature then raised to dull redness for 5 minutes. The product is extracted with water, 25–31 c.c. of sulphuric acid (1 : 1) added, and the solution concentrated to 100 c.c., when 1 gram of potassium iodide is added and the liquid boiled down to 40 c.c. After destroying any trace of iodine with a few drops of sulphurous acid, the solution is diluted considerably with hot water, and the arsenic precipitated as sulphide. The precipitate, after washing three times with hot water, is dissolved with 20 c.c. of $N/2$-sodium hydroxide, and the filtered solution treated with 30 c.c. of hydrogen peroxide (20 vols.), the excess of this reagent being destroyed by heating on the water-bath. A few drops of phenolphthalein are added followed successively by 11 c.c. of sulphuric acid (1 : 1) and one gram of potassium iodide; the solution is evaporated down to 40 c.c. and the pale-yellow colour removed by sulphurous acid. Cold water is then added, and the diluted solution neutralised with $2N$-sodium hydroxide, and just acidified with sulphuric acid. The arsenite solution is now titrated with standard iodine solution and starch in the presence of sodium hydrogen carbonate or sodium phosphate (Little, Cahen, and Morgan, Chem. Soc. Trans. 1909, 95, 1477).

Antimony. When present in organic compounds, this element may be estimated by acidifying the product of the sodium peroxide fusion (*v. Arsenic, supra*), and precipitating as sulphide, this precipitate being collected, washed, and weighed in the manner indicated under *Gravimetric determinations*.

Oxygen. No satisfactory method has yet been devised for the direct determination of this

element, and it is usually estimated by difference (*v.* v. Baumhauer, Annalen, 90, 228 ; Zeitsch. anal. Chem. 5, 141 ; Stromeyer, Annalen, 117, 247 ; Mitscherlich, Zeitsch. anal. Chem. 6, 136 ; 7, 272 ; 13, 74, and 15, 371 ; Ladenburg, Annalen, 135, 1 ; Maumené, Compt. rend. 55, 432 ; and Cretin, Zeitsch. anal. Chem. 13, 1).

Proximate analysis of carbon compounds.

The methods to be adopted for the separation of the constituents of any particular mixture will depend entirely upon the nature of the mixture. It is only possible to describe the general methods which are found to be most useful in organic analysis. To a certain limited extent these operations are applicable to the proximate analysis of complex inorganic mixtures.

Fractional distillation is available for the separation of liquids which differ considerably in their boiling points (*v.* DISTILLATION).

Distillation in a current of steam is frequently employed as a method of proximate analysis. In this way volatile organic acids can be separated from volatile bases by steam-distilling the mixture in the presence of mineral acids. On the other hand, volatile bases are separated from organic acids by distilling in steam the mixture of these substances rendered alkaline by sodium or potassium hydroxide.

Fractional precipitation may be employed for the separation of substances, some of which are precipitated by a given reagent, whilst the others are not : or for the separation of substances which differ in the *order* of their precipitation. If, for example, silver nitrate is added in successive small quantities to a solution containing an iodide, bromide, and chloride, the first portion of the precipitate contains the greater part of the iodine ; the middle portion contains the greater part of the bromine ; and the last portion the greater part of the chlorine. In a similar manner organic acids can, not unfrequently, be separated by taking advantage of differences in the order of their precipitation by silver nitrate or lead acetate. In these cases the separated precipitates can be suspended in water and decomposed by hydrogen sulphide, when the acids are again liberated.

Fractional crystallisation may be adopted in the case of substances which differ in their solubility in one and the same solvent. The solution is concentrated somewhat, and the crystals which separate are removed ; the mother liquor is still further concentrated, and the second crop of crystals is removed, this process being repeated as often as the case demands. The least soluble compound is mainly in the first crop of crystals ; the most soluble is in the last mother liquor.

Fractional saturation is an analogous process, but is of more limited application. It was employed by Liebig for the separation of volatile organic acids. The mixture of acids is mixed with a quantity of caustic soda or potash insufficient for complete saturation, and is then distilled. The acids of higher molecular weight are first neutralised and converted into salts, which of course remain in the retort, whilst the acids of lower molecular weight are found in the free state in the distillate. Anything like complete separation is only to be obtained by many repetitions of this process.

Fractional solution.—The most useful and most generally applicable method of proximate analysis is based upon the different solubilities of various substances in different menstrua. The mixture is treated successively with various solvents, each of which dissolves some of the constituents, but leaves the others undissolved. Advantage may also be taken of the fact that the solubilities are in many cases modified by a rise of temperature. Further, if two substances differ considerably in their solubility in one and the same liquid, they may be separated by treatment with successive small quantities of the liquid, which removes the more soluble compound but leaves the greater part of the other undissolved. The following is a list of the solvents commonly employed, with indications as to their general properties :—

Water dissolves many salts and acids ; inorganic and organic alkalis and their salts ; carbohydrates, gums, certain alcohols, polyhydric phenols, and other highly oxidised carbon compounds which are not readily soluble in alcohol, ether, &c. On the other hand, it does not dissolve the carbonates, phosphates, oxalates, and certain other salts of the heavier metals. Very many organic substances are insoluble in this liquid. It decomposes the halogen compounds of the acid radicles and certain other compounds, and converts many normal metallic salts into basic salts, part of the acid passing into solution in the free state.

Dilute acids will dissolve many salts, and also some organic substances which are insoluble in water.

Alcohol dissolves many salts, caustic alkalis, hydrocarbons, fatty acids, resins, and a very large number of carbon compounds. It reacts with many haloid substitution derivatives, and hence is not a suitable solvent for this class of compounds.

Ether dissolves a few salts, and is an excellent solvent for hydrocarbons, fats, resins, alkaloids, and almost all organic compounds which are insoluble in water. It reacts with very few substances, and boils at a low temperature, so that it can readily be distilled off and the dissolved substance recovered.

Benzene dissolves iodine, sulphur, phosphorus, oils, fats, wax, camphor, resins, caoutchouc, gutta-percha, &c., and is especially useful as a solvent for haloid derivatives, on which it has no action. In certain instances this hydrocarbon may be replaced by its homologues, toluene, and the xylenes.

Carbon disulphide shares with ether the advantage of being readily volatile. It should always be purified from dissolved sulphur before being used. The best plan is to mix it with a small quantity of white wax, and then distil off the disulphide on a water-bath. It dissolves sulphur, phosphorus, iodine, fats, essential oils, resins, caoutchouc, &c. ; but its solvent powers are comparatively limited, and almost all salts and very many carbon compounds are insoluble in it.

Light petroleum consists of the more volatile hydrocarbons of the paraffin series. It occurs in commerce in several varieties under different names. *Petroleum ether* boils at 50°–60° ; *petroleum benzene*, at 70°–90° ; *ligroïn*, at 90°–120°. They are excellent solvents for oils and fats, but

dissolve very few other compounds. Three grades of light petroleum are now obtainable for use as solvents, boiling respectively at 40°–60°, 60°–80°, and 80°–100°.

Chloroform readily dissolves oils, fats, and similar substances, and is especially useful as a solvent for alkaloids.

The chloro- derivatives of ethane and ethylene have been introduced as useful non-inflammable solvents for oils, fats, or resins; these liquids give a wide range of boiling-points and solvent action (Koller, 7th Congress Applied Chemistry, 1909). A large number of other solvents are applied in certain special cases, and among those more commonly employed may be mentioned, acetone, ethyl acetate, amyl alcohol, pyridine, aniline, and nitrobenzene.

The treatment of a solid with a volatile solvent must be conducted in a special apparatus, especially if the liquid is to be heated. Various forms of apparatus have been devised for this purpose, but there is none more efficient than that of Soxhlet (Dingl. poly. J. 232, 461). It consists of a short wide test tube (E), open at the top but closed at the bottom, to which is sealed a narrower tube (N) which can be fitted
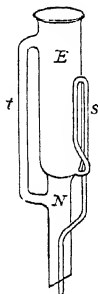
FIG. 29.   FIG. 30.

into a small weighed flask by means of a cork. Communication between the two tubes is made by means of (1) a narrow side tube (s) which opens into the bottom of the wider upper tube, forms a siphon, and descends through the lower tube nearly to the bottom of the flask; and (2) a wider side tube (t) which enters the upper tube near the top and the lower tube near the junction (Fig. 29). A weighed quantity of the substance to be treated is placed in a cylinder of filter paper open at the top, and introduced into the upper tube, or the bottom of the tube is packed with purified cotton wool, and the substance is placed upon this. A quantity of the solvent rather more than sufficient to fill the upper tube to the level of the bend in the siphon, is placed in the flask and heated to boiling by means of a water-bath. The upper tube is attached to a reflux condenser, care being taken that the condensed liquid falls directly into the cylinder containing the substance. The vapour passes up the wide side tube, is condensed, falls upon the substance, and filters through the paper or cotton wool. As soon as the liquid rises to the

bend of the siphon, the latter draws off the clear solution into the flask, and the liquid is again volatilised whilst the dissolved matter remains in the flask. The process goes on automatically, and the substance can be extracted many times with a small quantity of liquid. When extraction is complete, the flask is connected with an ordinary condenser, the liquid is distilled off, and the residue dried and weighed if necessary.

A convenient apparatus for treatment with solvents in dishes has been described by A. W. Blyth (Chem. Soc. Trans. 1880, 37, 140).

In many cases substances in solution can be removed and separated by agitating the liquid with some non-miscible solvent. The alkaloids and many amines can be removed from aqueous solutions by means of ether, whilst metallic salts are left; fatty substances can be removed from liquids by means of light petroleum, and so on. Extractions of this kind are best made in a separator consisting of a somewhat wide tube contracted at one end, which is fitted with a cork or stopper, whilst the other end is drawn out into a narrow tube provided either with a stop-cock or an indiarubber tube and a pinch-cock (Fig. 30). The liquid and the solvent can be completely mixed by agitation, and after they have separated the lower layer can be drawn off. If it is required to remove the supernatant liquid in this or any similar case, a somewhat narrow tube is bent twice at right angles, and one limb is fitted by means of a cork into a distilling or other flask, which is connected with an aspirator, whilst the other limb of the tube is placed in the liquid. When the aspirator is set in action, the liquid is drawn over into the flask, from which it can be distilled. With care a very accurate separation can be made, and the tube is readily rinsed by drawing some of the fresh solvent through it. This method may be rendered approximately quantitative by calibrating the above cylindrical separator (Fig. 30).

The microscope is of the greatest service in ascertaining whether a substance is a single compound or a mixture, and a microscopic examination of the various products obtained in the course of a proximate analysis affords valuable information as to the extent to which separation has been effected.

ESTIMATION OF RADICLES COMMONLY OCCUR-RING IN ORGANIC COMPOUNDS.

In this section it is only possible to indicate briefly a few of the most general methods by which certain typical radicles present in organic compounds can be estimated.

Hydroxyl. A known weight of the hydroxylic compound is treated with excess of magnesium methyl iodide (Grignard's reagent), and the amount of methane evolved is measured in a gas burette (Fig. 31).

$$R \cdot OH + CH_3 \cdot MgI = R \cdot OMgI + CH_4.$$
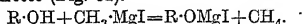
The organic magnesium compound is dissolved in dry amyl ether or phenetole, and if the hydroxylic compound is too insoluble in either of these solvents, it may be dissolved in dry pyridine.

(Hibbert and Sudborough, Chem. Soc. Trans. 1904, 85, 933; and Zerewitinoff, Ber. 1907, 40, 2023.)

This process has been extended to the estimation of sulphydryl- (SH), imino-, and

amino- groups, and for all active hydrogen atoms (*cf.* Ber. 1908, 41, 2233 and 3025).
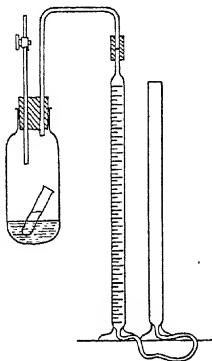
FIG. 31.

Methoxyl.

The estimation of methoxyl, a radicle present in many naturally occurring organic compounds, is generally accomplished by Zeisel's method, which consists in heating the substance with concentrated hydriodic acid or with a mixture of this acid and acetic anhydride. Methyl iodide is evolved and absorbed in alcoholic silver nitrate, with the result that silver iodide is precipitated, each molecular proportion of this substance being equivalent to one
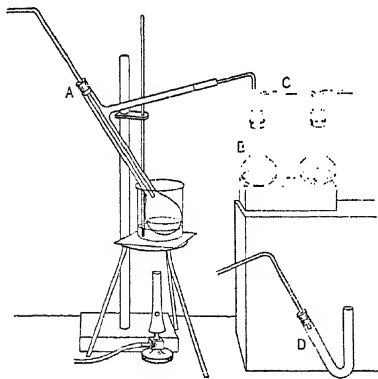
FIG. 32.

methoxyl group. Zeisel's original apparatus (Monatsh. 1885, 6, 989; 1886, 7, 406) has been modified subsequently by several investigators (M. Bamberger, Monatsh. 1894, 15, 904; Perkin, Chem. Soc. Trans. 1903, 83, 1367; Hesse, Ber. 1906, 39, 1142; Decher, Ber. 1903, 36, 2895; Hewitt and Moore, Chem. Soc. Trans. 1902, 81, 318). Of these modifications Perkin's (Fig. 32) is probably the simplest; it consists of a distilling flask, A, with a very long neck (20–25 cm.)

heated in a glycerine bath at 130°–140°, a current of carbon dioxide being passed through the mixture of substance and concentrated hydriodic acid. The heating is continued for one hour, and the temperature finally raised, so that the hydriodic acid boils gently, but without distilling into the side tube of the distilling flask. The methyl iodide is collected in two flasks, B, containing alcoholic silver nitrate. The precipitated silver iodide is treated with nitric acid, the alcohol evaporated, and the precipitate collected and weighed in the usual manner.

Zeisel's method and its modifications are applicable to the estimation of ethoxyl, but the results obtained are generally less accurate.

Methyl.

A further modification of Zeisel's method renders it available for the estimation of methyl groups attached to nitrogen. The substance is heated with concentrated hydriodic acid and dry ammonium iodide, and the methyl iodide evolved dealt with in the manner indicated above (Herzig and H. Meyer, Ber. 1894, 37, 319; Monatsh. 1894, 15, 613; 1895, 16, 599; 1897, 18, 379; Kirpal, Ber. 1908, 41, 820).

Acetyl.

It is only possible in comparatively few cases to determine with certainty by ultimate analysis the number of acetyl groups existing in organic compounds. For example, the mono-, di-, and tri- acetyl derivatives of the trihydroxybenzenes have approximately the same percentage composition. These and other similar acetyl derivates are hydrolysable by standard caustic alkalis employed in alcoholic solutions, even when they are not readily attacked in aqueous solutions (Benedikt and Ulzer, Monatsh. 1887, 8, 41; Van Romburgh, Rec. trav. chim. 1882, 1, 48; R. Meyer and Hartmann, Ber. 1905, 38, 3956). Acid hydrolysis may be employed in a large number of cases and the volatile acetic acid distilled into standard alkali, the excess of which is determined by alkalimetry. According to Wenzel's process, the acetyl derivative is first hydrolysed by moderately strong sulphuric acid (1 : 2H₂O), and the mixture treated with monosodium phosphate and boiled down to dryness; the sulphuric acid is fixed as sodium sulphate, and the acetic acid is distilled into a known excess of standard alkali, the distillation being carried out under reduced pressure (Monatsh. 1893, 14, 478; 1897, 18, 659).

The destructive action of strong sulphuric acid on organic compounds may be avoided by the use of the aromatic sulphonic acids as hydrolytic agents. The acetyl compound is distilled in steam in a 10 p.c. solution of benzenesulphonic acid or one of the naphthalenesulphonic acids; the distillate, which contains all the acetic acid furnished by the hydrolysis, is titrated with standard barium hydroxide (Sudborough and Thomas, Chem. Soc. Trans. 1905, 87, 1752).

A. G. Perkin hydrolyses the acetyl compound with alcoholic sulphuric acid, adding fresh alcohol from time to time. The ethyl acetate obtained in the distillate is then hydrolysed with a known amount of standard caustic alkali, and the excess of the latter ascertained with standard acid (Chem. Soc. Trans. 1904, 85, 1462; 1905, 87, 107; 1907, 91, 1230).

Carboxyl.

In many cases the number of carboxyl (CO_2H) groups in an organic compound can be determined by the analysis of its neutral salts. For this purpose the silver salts are generally selected, as they are usually anhydrous, and indicate the normal basicity of the organic acid. The aromatic hydroxy-carboxylic acids (*e.g.* 1 : 5-dinitro-*p*-hydroxybenzoic acid) take up two atoms of silver, one replacing the carboxylic, and the other the phenolic hydrogen. Some silver salts of organic acids are sensitive to light, and others are very explosive. The more stable ones can be analysed by direct ignition and weighing the residual silver. In other cases the organic matter must be destroyed with nitric acid, and the silver estimated as chloride in the acid liquid.

Other metallic salts are frequently employed in determining the basicity of carboxylic acids, and it is advisable before arriving at a final conclusion to estimate the metals in a series of these compounds.

If the molecular weight of a carboxylic acid is known, the basicity can often be determined by titration with aqueous or alcoholic sodium, potassium, or barium hydroxide; the indicators generally employed are phenolphthaleïn, methyl orange, and lacmoid.

The following indirect method has been recommended (P. C. McIlhiney, Amer. Chem. J. 1894, 16, 408) for the estimation of carboxyl groups. The substance (1 gram) is dissolved in excess of alcoholic potash, the alcohol being at least 93 p.c. The solution is saturated with carbon dioxide until the excess of alkali is precipitated as carbonate or bicarbonate. The precipitate is collected and washed with alcohol, the filtrate is distilled to remove the solvent, and the residue containing the potassium salt of the organic acid is distilled with 10 p.c. aqueous ammonium chloride, the ammonia evolved being estimated in the usual way. Each molecular proportion of ammonia corresponds with one carboxyl group. This method is applicable to the weaker fatty acids.

Carboxyl can be estimated by a method based on the following reaction :—

$$6R \cdot CO_2H + 5KI + KIO_3 = 6R \cdot CO_2K + 3I_2 + 3H_2O$$
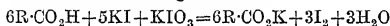
The weighed substance is digested for 12 hours with an aqueous solution of pure potassium iodide and iodate in a stoppered vessel. The mixture containing the liberated iodine is rinsed unto the generating vessel of a gas volumeter and treated with alkaline hydrogen peroxide, when the oxygen evolved

$$I_2 + 2KOH + H_2O_2 = 2KI + 2H_2O + O_2$$
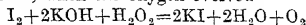
is a measure of the carboxyl groups originally present ($6CO_2H \equiv 3O_2$) (Baumann-Kux, Zeitsch. anal. Chem. 1893, 32, 129 ; Annalen, 1904, 335, 4; *cf.* Gröger, Zeitsch. angew. Chem. 1890, 3, 353, 385). It should be noticed that acidic substances not containing carboxyl groups (*e.g.* picric acid) liberate iodine from the iodide-iodate mixture.

Carbonyl.

The carbonyl group, whether present in aldehydes $R \cdot CO \cdot H$ or ketones $R \cdot CO \cdot R'$, can be detected by means of the following colour-reaction. An aqueous or alcoholic solution of the substance is treated with a 0·5 to 1 p.c. solution of the hydrochloride of an aromatic meta-diamine (meta-phenylenediamine or its homologues), when in a few minutes an intense green fluorescence is developed, which attains its maximum intensity after two hours. All aldehydes give this reaction, but the mixed ketones and ketonic acids do not (Windisch, Zeitsch. anal. Chem. 1888, 27, 514).

Practically all aldehydes restore the colour to the following solution (Schiff's reagent). A litre of 0·10 p.c. magenta solution is decolourised by adding 20 c.c. of sodium bisulphite solution (30°Bé.) followed after one hour by 10 c.c. of concentrated hydrochloric acid. (For the exceptions, *cf.* Bittó, Zeitsch. anal. Chem. 1897, 36, 375.) The reaction has also been utilised quantitatively (McKay Chase, J. Amer. Chem. Soc. 1906, 28, 1472; Schimmel & Co., Ber. 1907, 123).

Phenylhydrazine condenses with aldehydes and ketones, yielding phenylhydrazones. When the mixture is treated with Fehling's solution (70 grams $CuSO_4, 5H_2O$, 350 grams Rochelle salt, and 260 grams KOH, in 2 litres), the excess of phenylhydrazine is decomposed, evolving nitrogen :

$$C_6H_5 \cdot NH \cdot NH_2 + O = C_6H_6 + H_2O + N_2,$$
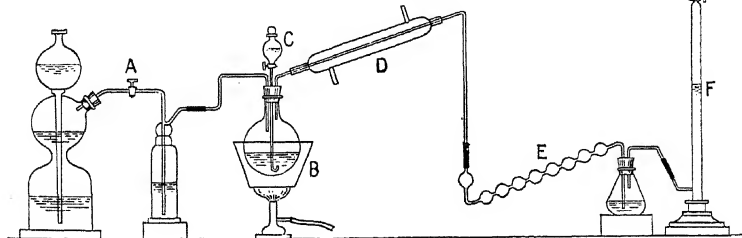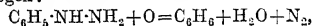
Fig. 33.

while the phenylhydrazone remains unchanged. The estimation is carried out in a flask, B, connected with a carbon dioxide generator, A (Fig. 33). A known volume of Fehling's solution is introduced and covered with a layer of petroleum to prevent the caustic potash from absorbing the carbon

dioxide. A blank experiment is first made with the standard solution of phenylhydrazine hydrochloride and aqueous sodium acetate, the nitrogen evolved on heating the solutions together being collected in a Schiff's nitrometer, F. The experiment is then repeated with the same solutions of phenylhydrazine and sodium acetate *plus* the carbonyl compound; the difference between the two volumes of nitrogen collected is a measure of the carbonyl present in the compound (Strache, Monatsh. 1891, 12, 524; 1892, 13, 299; 1893, 14, 270; Watson Smith, Chem. News, 1906, 93, 83).

When the carbonyl compound (*e.g.* pyruvic acid) condenses readily with phenylhydrazine or its hydrochloride in aqueous solution, the excess of this base can be estimated by adding excess of $N/10$-iodine solution, and titrating the remaining iodine with standard sulphurous acid or thiosulphate, using starch as indicator. This estimation is based on the following reaction :—

$$C_6H_5 \cdot NH \cdot NH_2 + 2I_2 = 3HI + C_6H_5I + N_2.$$
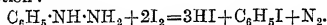
The phenylhydrazone is not affected by the iodine solution (E. v. Meyer, J. pr. Chem. 1887, [2] 36, 115; *cf.* Petrenko-Kritschenko, Ber. 1901, 34, 1699; and Annalen, 1905, 341, 15, 150).

Organic amines.

The organic amines are divisible into three primary, secondary, and tertiary, containing their nitrogen atoms combined respectively with one, two, and three organic groups. These groups may be either aliphatic or aromatic, and the reactions of each of the three classes of amines depend very largely on the nature of the organic groups to which the basic nitrogen atom is attached.

Primary amines. The primary amino-group $C \cdot NH_2$ may be detected by the carbyl-amine reaction (Hofmann, Ber. 1870, 3, 767), irrespective of the nature of the organic group, which may be either aliphatic, aromatic, or hydroaromatic (*cf.* Monatsh. 1896, 17, 397). The test consists in warming the substance in alcoholic solution with chloroform and caustic potash, when a carbylamine (iso-nitrile) is produced, which has a pungent disagreeable odour :

$$R \cdot HN_2 + CHCl_3 + 3KOH = R \cdot NC + 3KCl + 3H_2O.$$
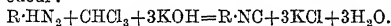
The primary amines all interact with nitrous acid, but the aliphatic bases are immediately converted into hydroxyl derivatives (alcohols), whereas the aromatic bases furnish diazo-derivatives from which the nitrogen is evolved rapidly on warming or slowly at the ordinary temperature.

In the case of the aliphatic primary amines, this nitrogen can be collected, and the amount indicates the proportion of amino- groups present. As nitrous acid itself decomposes readily, evolving oxides of nitrogen, Staněk recommends the use of nitrosyl chloride, obtained by adding fuming hydrochloric acid to 40 p.c. aqueous sodium nitrite (Zeitsch. physiol. Chem. 1905, 46, 263). This reagent can be mixed with saturated salt solution without undergoing decomposition ; the aliphatic amino-carboxylic acids (glycine, &c.) can be readily decomposed by it in a current of carbon dioxide, and the nitrogen evolved is freed from the former gas

and traces of oxides of nitrogen by passing the mixed gases through alkaline permanganate solution. Half the nitrogen measured in the gas burette corresponds with that originally present in the amino-acid.

In the case of the aromatic primary amines, the acid solution of the base is carefully diazo-tised at 0° with standard sodium nitrite ; the end-point is reached when a drop of the solution gives a blue colour on starch-iodide paper. The sodium nitrite solution may be standardised with either potassium permanganate, sodium sulphanilate ($NH_2 \cdot C_6H_4 \cdot SO_3Na, 2H_2O$) or para-toluidine (*cf.* Green and Rideal, Chem. News, 1884, 49, 173 ; Kinnicutt and Nef, Amer. Chem. J. 1886, 5, 388 ; Zeitsch. anal. Chem. 1886, 25, 223).

Estimation of imino-groups in secondary amines. A weighed quantity of the substance is mixed with a known excess of acetic anhydride, either alone or diluted with dry xylene or dimethylaniline (Bull. Soc. chim. 1892, [3] 7, 142 ; Chem. Zeit. 1893, 17, 27, 465). After one hour, water is added and the mixture warmed under a reflux apparatus, so that no anhydride is lost by evaporation. The solution is then titrated with standard barium hydroxide and phenolphthaleïn indicator. The amount of acetic acid present indicates the excess of acetic anhydride left over from the acetylation of the secondary base.

The tertiary amines and the quaternary ammonium salts do not give the reactions of the primary and secondary amines, but the total amount of basic nitrogen present in an organic amine can frequently be ascertained by the analysis of the characteristic salts of the base. The aurichlorides and platinichlorides may frequently be employed for this purpose, as these double salts on ignition leave a residue of the metal, each atomic proportion of gold corresponding to one basic nitrogen atom, while a similar quantity of platinum corresponds with two basic nitrogen atoms. In the majority of cases these double salts have respectively the general formulæ, $R \cdot HCl, AuCl_3$ and $(R \cdot HCl)_2 PtCl_4$, and are obtained in the anhydrous condition ; yet, in certain instances, hydrated forms are known and sometimes the salts themselves have an anomalous composition not corresponding with the general formulæ. Evidence obtained in this way should, if possible, be supplemented by the analysis of other salts, and for this purpose the ferrichlorides, chromates, oxalates, thiocyanates, ferrocyanides, picrates, and picrolonates have been employed, as well as the commoner nitrates, sulphates, and halide salts.

Gas analysis.

The experiments of Gay-Lussac established long ago the value, from a scientific point of view, of the determination of the volumetric composition of gases and the products formed by their interaction ; but it is only within recent times that the methods of gas analysis have been applied to any great extent for technical purposes. The value of such determinations is now generally recognised on account of the information which they give respecting the efficiency of combustion, the progress of operations in which gases are consumed or produced, and the like.

With few exceptions the volumetric and not the gravimetric composition of the gas is required, and the measurements are essentially measurements of volumes. The gas to be examined is confined over mercury or water in a suitable measuring apparatus, and its composition is determined (1) by treatment with appropriate absorbing reagents and measurement of the contraction produced ; (2) by exploding with oxygen or hydrogen and measuring the contraction ; (3) by exploding with oxygen or hydrogen, measuring the contraction, and then treating with absorbing reagents, and measuring the second contraction. Sulphur dioxide and some other gases soluble in water are estimated by titration, a definite volume of the gas being drawn through a measured quantity of a standard solution, the excess of which is afterwards determined.

The highly refined and accurate methods of gas analysis employed for purposes of research are of little value for technical purposes on account of the length of time required for their execution. Information respecting these methods may be found in Bunsen's Gasometrische Methoden, 2nd ed. 1887 ; Sutton's Volumetric Analysis, 9th ed. 1904 ; Dittmar's Exercises in Quantitative Analysis, 1887 ; Hempel's Gasanalytische Methoden, 3rd ed. 1900 ; Travers' Experimental Study of Gases, 1901 ; *v*. also Thomas (Chem. Soc. Trans. 1879, 35, 213), and Meyer and Seubert (Chem. Soc. Trans. 1884, 45, 581). In this article only those methods will be described which are available for technical purposes.

Measurements.—The volume which a given mass of gas occupies depends on the temperature, the pressure, and the proportion of moisture which it contains. The temperature is ascertained by means of a thermometer attached to or suspended near to the measuring vessel. Measurements are usually made under atmospheric pressure, and this is determined by means of a barometer placed in the room in which the analysis is made. The siphon barometer is a convenient form of instrument for the purpose, and should stand on the table close to the gas apparatus. In case the level of the mercury or water in the measuring tube is higher than that in the trough or the attached tube, the true pressure upon the gas is given by the height of the barometer *minus* the difference between the mercury level inside and outside the tube. If water is used, the height of the water column divided by 13·6 gives the height of the corresponding column of mercury with sufficient accuracy. It is better to eliminate this correction by adjusting the liquid so that it is at the same level both inside and outside the tube, which is easily done.

The gas must be either perfectly dry or saturated with moisture. If an indefinite quantity of water vapour is present, accurate measurements are impossible. It is more convenient to measure the gas when moist, and hence if the gas is confined over mercury a few drops of water are introduced when the tube is filled with the mercury and this water is taken up by the gas. Under these conditions the surrounding pressure is balanced partly by the gas and partly by the aqueous vapour which it contains, and in order to ascertain the pressure which the gas itself is under, the tension of aqueous vapour at the particular temperature must be subtracted from the height of the barometer. The formula for reducing the volume of gas to the standard temperature and pressure ($0°$ and 760 mm.) is :

$$V_0 = \frac{V + 273 \times (B - f)}{(273 + t) \times 760} \text{ or } V_0 = \frac{V \times (B - f)}{(1 + 0.00366t \times 760)}$$

in which V is the actual reading ; t, the temperature ; f, the tension of aqueous vapour at the temperature, t ; and B, the height of the barometer. The reduction of the height of the barometer to $0°$ is necessary for accurate calculation, but may usually be omitted. The following table, abbreviated from Bunsen's Gasometrische Methoden, gives the value of $1 + 0.00366t$ for the ordinary range of temperature :—

$t°$	Number	Log	$t°$	Number	Log	$t°$	Number	Log
$0°$	1·00000	0·00000	$11°$	1·04026	0·01714	$21°$	1·07686	0·03216
1	1·00366	0·00159	12	1·04392	0·01867	22	1·08052	0·03363
2	1·00732	0·00317	13	1·04758	0·02019	23	1·08418	0·03510
3	1·01098	0·00474	14	1·05124	0·02170	24	1·08784	0·03656
4	1·01464	0·00631	15	1·05490	0·02321	25	1·09150	0·03802
5	1·01830	0·00788	16	1·05856	0·02471	26	1·09516	0·03948
6	1·02196	0·00943	17	1·06222	0·02621	27	1·09882	0·04093
7	1·02562	0·01099	18	1·06588	0·02771	28	1·10248	0·04237
8	1·02928	0·01253	19	1·06954	0·02921	29	1·10614	0·04381
9	1·03294	0·01407	20	1·07320	0·03068	30	1·10980	0·04524
10	1·03660	0·01561						

When the estimations are made rapidly, and only approximate results are required, the corrections for temperature and pressure are omitted, since it may be assumed that they remain constant during the analysis.

The following plan, described by Winkler, renders the use of the barometer and thermometer unnecessary, and makes the calculation much simpler. It is an adaptation of William-son and Russell's method of always measuring the volume of the gas at the same degree of elasticity. A tube about 1 metre long, closed at one end and graduated to 120 c.c. in tenths, is moistened internally with a few drops of water, and mercury is poured in in such quantity that when the tube is inverted the mercury stands somewhat higher than 100. The volume which 100 c.c. of air measured at standard temperature

and pressure should occupy under the conditions described, is calculated from the expression:

$$V = \frac{(760-4\cdot5)100\times(273+t)}{273(B-f)} \text{ or } \frac{(760-4\cdot5)100\times1+0\cdot00366t)}{B-f}$$

and air is carefully introduced into the tube until, when the mercury is at the same level inside and outside the tube, it stands exactly at the calculated volume. The tube now contains a quantity of gas saturated with moisture, which, under standard conditions, would occupy 100 c.c., but its actual volume varies in the same ratio as the volume of gas to be measured. The two tubes are allowed to stand side by side, and when the levels have been properly adjusted in each case the volume of the gas to be measured and the volume of the air in the comparison tube are read off. The volume (under standard conditions) of the gas under examination is obtained by the proportion

$$V : V_0 : : V_1' : V_0',$$

in which V is the actual volume of air in the comparison-tube; V_0, its volume under standard conditions, which is always 100; V_1', the observed volume of the gas to be measured; and V_0', its volume under standard conditions.

During the operations the temperature should be kept as constant as possible, and the readings should be taken rapidly, otherwise the proximity of the body will cause variations in the temperature of the gas. It is an advantage to have the measuring tube surrounded by a wider tube which is filled with water. The most accurate method is to take the readings through a carefully levelled telescope (a cathetometer) at a distance of about five or six feet. This also avoids parallax. The measuring tube must be kept vertical, and when water is the confining liquid, sufficient time must be given for the liquid to run down the sides of the tube. Not unfrequently this requires several minutes.

Reagents.

All liquid reagents should be saturated with the gases which they do not absorb chemically. It is desirable that the tensions of these gases in the liquids should be approximately equal to their tensions in the gases which are to be analysed, in order to avoid exchanges between the gas and the absorbing liquid. This is best secured by going through the process two or three times without making measurements, whenever the pipettes have been freshly filled. Liquids used for the analysis of, say, flue gases, should not be used for gases of a different character, *i.e.* which contain the constituents in very different proportions.

Bromine water is used for absorbing olefines. It should be well saturated with bromine and kept in the dark.

Cuprous chloride is made by dissolving 50 grams of cupric oxide in hydrochloric acid, adding 50 grams of copper, and boiling for some time with as little exposure to air as possible. The solution is then diluted to 1000 c.c. with hydrochloric acid of sp.gr. 1·12, and allowed to remain in contact with metallic copper in a closed vessel until the solution becomes colourless. This solution attacks mercury rapidly.

Cuproso-ammonium chloride, obtained by dissolving cuprous chloride in ammonia, does not attack mercury.

The stock solution is made by dissolving 200 grams of cuprous chloride and 250 grams of ammonium chloride in 750 c.c. of water; it is kept in stoppered bottles, and, when required, mixed with one-third its volume of ammonia solution (sp.gr. 0·91).

Hydrogen is obtained by the action of dilute sulphuric acid on pure zinc. The granulated zinc may be placed in a small bottle fitted with a capillary delivery tube, which can be closed by a tap or pinch-cock. The bottle has a tubulus at the bottom, and is connected by a caoutchouc tube with a similar bottle containing dilute sulphuric acid. The latter bottle is raised so that the acid runs on the zinc, and the action is allowed to proceed until the air is completely expelled from the first bottle. The tap is then closed, and the acid is driven back into the second bottle by the pressure of the hydrogen. It is advisable to keep the second bottle at a slightly higher level than the first, to avoid any chance of air leaking in. One of Hempel's tubulated absorption bulbs answers admirably (Fig. 41). The zinc is attached to a cork, which is inserted in the tubulus of the first bulb, and the acid is introduced. When all air is expelled, the capillary tube is closed, and the acid is driven up into the second bulb, so that the pipette is always charged with hydrogen under pressure.

Oxygen is obtained in a pure state by heating potassium chlorate *without* manganese dioxide. The powdered chlorate is contained in a glass bulb, the neck of which is drawn out to form a narrow delivery tube.

Phosphorus is employed in the form of narrow sticks, which are made by melting it under warm water and drawing it up into narrow glass tubes. The upper ends of the tubes are closed by the finger, and they are plunged into cold water, when the phosphorus solidifies. It may also be used in a granular form, obtained by shaking the phosphorus vigorously with warm water in a well-closed flask until it solidifies.

Caustic potash (or soda) for Orsat's apparatus is dissolved in three parts of water, and the solution kept in well-stoppered bottles. Hempel uses a solution of caustic potash in two parts of water, which will absorb forty times its volume of carbon dioxide. It may, however, be used somewhat more dilute, and is then less liable to attack the glass.

Pyrogallol is kept in the solid state, and only dissolved immediately before being used. Orsat recommends a solution of 25 grams of pyrogallol in a small quantity of hot water, mixed with 150 c.c. of a solution of 1 part of caustic soda in 3 parts of water. Hempel uses a mixture of 25 c.c. of a 20 p.c. solution of pyrogallol with 75 c.c. of 33·3 p.c. caustic potash solution. This quantity will absorb 200 c.c. of oxygen.

Sulphuric acid of sp.gr. 1·84 is used as a drying agent and for the absorption of nitrogen oxides. Acid of the same strength mixed with so much sulphuric anhydride that it remains liquid at the ordinary temperature but solidifies if cooled, is used for absorbing ethylene and other hydrocarbons.

Water, which is very largely used for confining the gases, should be well saturated with air, but should not contain carbon dioxide. Distilled water is preferable, but any potable water of good quality may be used.

Standard solutions used in the estimation of gases by titration are known as *normal gas solutions* when they are of such strength that 1 c.c. of the solution is equivalent to 1 c.c. of the gas under standard conditions. A normal gas solution of iodine for the estimation of sulphur dioxide would contain 11·333 grams of iodine per litre, and the thiosulphate solution used in conjunction with it would be of equivalent strength.

In many cases it is the weight of the absorbed constituent per cubic metre or cubic foot of gas that is required, and the ordinary standard solutions may be used.

Methods of estimation.

Ammonia, by titration.

Benzene, by absorption in fuming nitric acid boiling at 86°, the nitrogen oxides being then removed by caustic potash. Fuming nitric acid also absorbs carbon dioxide and carbon monoxide. Like the olefines, benzene is absorbed by fuming sulphuric acid and by bromine water, and in fact no absorption method is at present known by means of which benzene and the olefines can be separated (Ber. 1888, 21, 3131).

Carbon dioxide, by absorption in potassium or sodium hydroxide.

Carbon monoxide, by absorption in a saturated solution of cuprous chloride in hydrochloric acid or ammonia. It seems (Ber. 1887, 20, 2754) that these solutions are liable to give off part of the dissolved carbon monoxide, especially after they have been used repeatedly. The error is less with the ammoniacal solution, and is reduced if the solution remains in contact with the gas for some time. The cuprous chloride solution should always be tolerably fresh, and should be saturated with hydrogen, nitrogen, and the other gases which usually occur with carbonic oxide (Ber. 1888, 21, 898). If the amount of carbon monoxide is small, it should be converted by combustion (*v. Hydrogen*) into carbon dioxide, which is afterwards absorbed by caustic potash. If the amount of carbon monoxide is large, the greater part may be absorbed by cuprous chloride, and the remainder removed by combustion and absorption.

The estimation of small quantities of carbon monoxide in air or other comparatively inert gases can be effected by passing the dried gas over solid iodine pentoxide. At temperatures varying from 40°–150° the following reaction occurs : $I_2O_5 + 5CO = 5CO_2 + I_2$. Either of the volatile products can be estimated : the iodine volumetrically by standard thiosulphate, or gravimetrically by absorption in a weighed tube containing copper powder ; the carbon dioxide may be absorbed in standard barium hydroxide, and the excess of the latter titrated with oxalic acid. If carbon dioxide is present in the gas under examination, it is first removed by potassium or barium hydroxide. Below 60° no hydrocarbon except acetylene reduces iodic anhydride. At higher temperatures several unsaturated hydrocarbons have an appreciable action. Ethylene hinders the oxidation of carbon monoxide by the iodine pentoxide. The process is applicable to air containing one part of carbon monoxide in 30,000, and is used for estimating the monoxide occluded in steel (Gautier, Compt. rend. 1898, 126, 871, 1299 ;

Jean, *ibid.* 1902, 135, 746 ; J. Amer. Chem. Soc. 1900, 22, 14 ; 1907, 29, 1589 ; Ann. Chim. anal. 1910, 15, 1).

Hydrogen is converted into water by combustion with air or oxygen, and the volume of the hydrogen is represented by two-thirds of the contraction consequent upon combustion. If the gas is confined over mercury, an excess of pure oxygen is introduced, the volume read off, and the pressure on the gas reduced considerably below atmospheric pressure by lowering the mercury in the level tube. The lower end of the explosion tube is closed, and combination is initiated by passing a spark from a coil between the platinum wires which are fused into the tube. The pressure is restored to the normal, and when the gas has cooled the volume is again read off.

When the gas is confined over water it is almost impossible to obtain satisfactory combustion, and it is much more convenient to pass the combustible mixture over gently heated spongy palladium. This is prepared by dissolving about two grams of palladium chloride in a small quantity of water, adding a small quantity of a saturated solution of sodium formate and sodium carbonate until the reaction is alkaline. About 1 gram of long and very soft asbestos fibres is introduced, and the pasty mass is dried at a gentle heat. In this way the asbestos is obtained covered with very finely divided palladium. After being completely dried at 100°, it is carefully washed with water to remove soluble salts and again dried. Some of the fibres are moistened and twisted into a thread about 1 cm. long, which is then introduced into the middle of a stout capillary tube, E, about 15 cm. long and 1 mm. internal diameter,
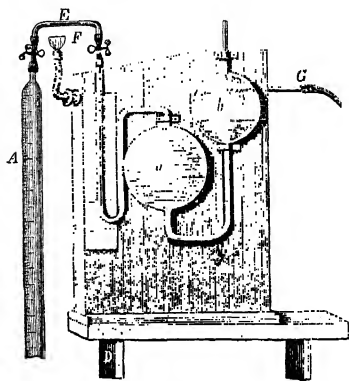
FIG. 34.

and this tube is bent at a right angle at each end. or in any other way convenient for its attachment to the measuring apparatus containing the gas. One end of the capillary is in communication with the graduated tube, A, and the other with a bulb pipette, C, filled completely with water, into which the gas is passed. A small gas or spirit-lamp flame is arranged to heat that part of the capillary which contains the asbestos. When the other gases have been estimated, the mixture of hydrogen and nitrogen which remains

is mixed with air by lowering the level-vessel until the pressure is sufficiently reduced, and then putting the measuring tube in communication with the air. The stop-cock is then closed, the asbestos very gently heated, and the gas passed slowly through the capillary into the bulb and back again three or four times. When combustion is complete, the volume of the residual gas is measured.

This method may be employed in estimating hydrogen in the presence of methane, since the latter is not burnt under these conditions, providing that the temperature does not exceed 500° (J. Soc. Chem. Ind. 1903, 22, 925; 1905, 24, 1202; Zeitsch. angew. Chem. 1903, 16, 695).

The palladinised asbestos can be used in promoting the combustion of carbon monoxide.

Drehschmidt (Ber. 1888, 21, 3245) prefers a platinum tube 20 cm. long and 2 mm. thick, with a bore 0·7 mm. diameter. The bore is almost closed by the insertion of a palladium wire extending through the whole length of the tube. The tube is attached to a burette and an absorption pipette in the same manner as the glass tube; 5 to 6 cm. are heated to redness by means of a gas flame, and the gas is passed backwards and forwards until there is no further alteration of volume. No explosions occur even with mixtures of hydrogen and oxygen containing only a slight excess of the latter.

Hempel has applied the well-known absorption of hydrogen by palladium to the estimation of this gas. Pure palladium is indifferent towards hydrogen in the presence of methane and nitrogen, but when it contains a little palladious oxide combustion of some of the hydrogen occurs, and the heat generated ensures the absorption of the remainder. Palladium sponge is heated and allowed to cool slowly so that it becomes superficially oxidised. A U-tube of 4 mm. internal diameter and 20 cm. total length is charged with 4 grams of this oxidised sponge and maintained at 90°–100° by immersion in a beaker of hot water; this tube is interposed between the gas burette and a pipette filled with water. The absorption is effected by siphoning the gas backwards and forwards through the palladium sponge.

Hydrogen chloride, by titration.

Hydrogen sulphide, by titration.

Hydrocarbons other than olefines are estimated by combustion, preferably with oxygen over mercury under reduced pressure. Acetylene and benzene may be burnt over palladium, but require a somewhat high temperature. Methane cannot be burnt in this way even in presence of hydrogen. The combustion of this gas is effected by mixing it with a considerable quantity of air and aspirating the mixture through a short tube containing cupric oxide heated to redness in a small combustion furnace, the carbon dioxide which is produced being absorbed in standard baryta solution, which is afterwards titrated with standard oxalic acid.

Drehschmidt finds (Ber. 1888, 21, 3249) that a mixture of methane and oxygen can readily be burnt in a platinum tube, as above, if the latter is heated to bright redness. The contraction is observed, and the carbon dioxide formed is removed and the volume again measured.

Nitric oxide is converted into peroxide by

admixture with oxygen, and the peroxide is absorbed by caustic potash, the excess of oxygen being afterwards absorbed by alkaline pyrogallate. Nitric oxide may also be absorbed by a concentrated solution of ferrous sulphate, but this method does not give such satisfactory results.

Nitrogen peroxide and nitrous anhydride, by titration; by absorption with sulphuric acid of sp.gr. 1·84; or, in absence of carbon dioxide and other absorbable gases, by absorption with caustic potash.

Olefines, by absorption with fuming sulphuric acid, acid vapours being removed by caustic potash; or by absorption in bromine water, bromine vapours being afterwards removed by caustic potash.

Oxygen, by absorption with alkaline pyrogallate. If the oxygen is present in greater proportion than 20 p.c. a small quantity of carbon monoxide is evolved from the pyrogallol during absorption, and hence the results are slightly too low. After treatment with pyrogallol the gas may be passed into the cuprous chloride bulbs in order to remove any carbon monoxide that may have been formed. Usually, however, this error has no material influence on the results. Oxygen may also be absorbed by phosphorus, and this has the advantage that the presence of carbon dioxide is without influence on the result. The temperature, however, must not be below 18°, and the absorption is prevented by the presence of ammonia, olefines, and other hydrocarbons, alcohol, &c.

Sodium hydrosulphite has been recommended as an absorbent for oxygen, the reaction

$$Na_2S_2O_4 + H_2O + O = 2NaHSO_3$$
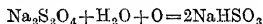
taking place readily at low or high temperatures. The solution contains 50 grams of the salt and 40 c.c. of sodium hydroxide (5 : 7) in 250 c.c. of water, and is used in a pipette filled with rolls of iron-wire gauze (Ber. 1906, 39, 2069).

Oxygen may also be estimated by combustion with hydrogen, either explosively by the spark or over palladium-asbestos. The hydrogen should be evolved from commercial ' pure ' zinc and pure dilute sulphuric acid, or in special cases from magnesium and sulphuric acid. One-third of the contraction consequent upon combustion gives the volume of the oxygen.

Sulphur dioxide, by titration.

In the ordinary gases from flues, generators, &c., the constituents are estimated in the following order : Carbon dioxide, olefines and benzene, oxygen, carbon monoxide, hydrogen, methane, nitrogen (as residue or by difference).

If acid vapours are present together with one or more of the above gases, the order of absorption, &c., must be determined by circumstances.

Apparatus and manipulation.

Collecting samples.—The gas to be analysed is usually drawn from the flue, chamber, &c., by aspirating it through glass tubes, which may be termed conducting tubes. When the temperature is high, porcelain tubes may be used ; or if the gas has no acid properties, iron tubes can be employed. When samples are constantly taken from the same flue, &c., it is convenient to have a short piece of porcelain or iron pipe cemented into the wall and closed at the outer end with a

plug, which is readily removed when the sample is taken. In cases where the gases are originally at a high temperature and possibly in a state of partial dissociation, it is important to draw the sample slowly through a somewhat long tube in order that the gas may cool slowly, since rapid cooling of the gases may leave them in a partially dissociated condition and thus lead to erroneous results.

The sample may be conveniently collected in the measuring apparatus itself ; but where this is not possible, a cylindrical glass tube A, drawn out at the upper end and connected with a stop-cock and capillary tube, and drawn out at the lower end and connected by caoutchouc tubing with a similar tube B, open at the top, makes a convenient sampler. The collecting tube may with advantage be provided with a stop-cock at the bottom. The vessel A is completely filled with water or mercury by raising B to a higher level, and the upper stop-cock is closed. The capillary tube is connected with the conducting tube, and the vessel B is lowered so that when the stop-cock is slowly opened the gas is drawn into A, and the water or mercury collects in B. When A is filled the stop-cocks are closed. The gas is readily transferred from A to the measuring vessel by raising B and carefully opening the stop-cock.

FIG. 35.

In all cases the air in the conducting tube must be expelled, and this is done by placing a T-tube between the end of the tube and the collecting vessel. This T-piece is connected with an aspirator, and the tube is filled with the gas before the stop-cock of the collecting vessel is opened. When the collecting vessel is provided with a three-way cock, the aspirator may be connected directly with the latter. Various forms of aspirator may be used. When the volume of gas to be aspirated is small (*e.g.* in removing air from the conducting tube), a small globular indiarubber aspirating pump is very convenient. For larger quantities of gas, glass
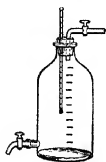
FIG. 36.   FIG. 37.

bottles with a tubulus or stop-cock at the bottom and a tube or stop-cock at the top, or similar vessels of sheet zinc, may be used (Figs. 36 and 37). They are filled with water, the upper tube being connected with the tube which passes into the flue, and the water is allowed to flow from the tap at the bottom. The volume of gas aspirated is determined by measuring the volume of water which flows from the aspirator, and correcting

this volume for temperature; &c., in the usual way (*v.* ASPIRATOR).

When aspiration is to be continued for a long time, one of the various forms of water pump may be used. The volume of air aspirated in a given time with a given pressure of water may be determined once for all by direct measurement, or a small gas meter may be placed between the pump and the vessel into which the gas is passed.

If the gas has to be kept for some time before analysis, or if it has to be transported from one place to another, it may be collected in glass tubes which have previously been drawn out at each end. As soon as the tubes are full, the ends are closed by stoppers of indiarubber tubing and glass rod, or are hermetically sealed by fusion. If the quantity of gas is large, cylindrical zinc vessels with conical ends closed by indiarubber corks answer very well.

(For other forms of gas-samplers, *v.* J. Soc. Chem. Ind. 1889, 8, 176 ; 1903, 22, 190.)

Estimations by titration.—A measured quantity of the appropriate standard solution is placed in a flask or a Woulff's bottle fitted with two tubes, one of which dips into the liquid and is connected with the tube placed in the flue, &c., whilst the other ends just below the cork and is connected with an aspirator. After aspiration has been continued for a sufficient length of time, the excess of reagent is determined by titration. The volume of gas aspirated is determined by the volume of water which has run from the aspirator or by means of a gauge attached to the aspirator. This volume of water, however, represents a volume of gas saturated with moisture and at a temperature and pressure which must be determined by means of a thermometer attached to the aspirator and a barometer in close proximity ; the volume under standard conditions is calculated in the usual way. In calculating the percentage composition of the gas, it must be borne in mind that the original volume of the gas was the sum of the volumes of the absorbed constituent and the volume which has passed into the aspirator.

If V_1 is the volume of the absorbed gas, and V_2 the volume which has passed into the aspirator, both under standard conditions, then

$$\frac{100 \times V_1}{V_1 + V_2} = \text{per cent. of } V_1 \text{ by volume.}$$

This method may be applied in the estimation of—

Ammonia, by absorption in sulphuric acid and titration with alkali.

Carbon dioxide (in small quantities), by absorption in standard baryta solution and titration with oxalic acid.

Chlorine, by absorption in a standard solution of arsenious oxide in sodium carbonate, and subsequent titration with iodine after saturating with carbon dioxide.

When hydrochloric acid and chlorine occur together, the latter is determined separately in one quantity, and a second quantity is absorbed in the solution of arsenious oxide in sodium carbonate free from chlorine, and the total chlorine is determined by titration with silver nitrate, using Volhard's thiocyanate method. In calculating the percentage composition, it is important to remember that 1 vol. of chlorine produces 2 vols. of hydrochloric acid.

Hydrochloric acid, by absorption in sodium carbonate and titration with silver nitrate, or, in absence of carbon dioxide and other acids, by absorption in standard caustic potash or soda, and subsequent titration with an acid.

Hydrogen sulphide, by absorption in standard iodine and titration with thiosulphate ; or by absorption in bromine water and gravimetric estimation as barium sulphate.

Nitrogen oxides, by absorption in acidified permanganate solution of definite strength, the gas being passed until the solution is just decolourised. This method gives the amount of nitrogen oxides in terms of their reducing power.

Sulphur dioxide, by absorption in standard iodine solution and titration with thiosulphate, or by absorption in bromine water and gravimetric estimation as barium sulphate. The latter plan may be adopted when the proportion of sulphur dioxide is very small and a large volume of gas must be aspirated.

Measuring and absorption apparatus.—Only those forms which have come into general use and are of wide applicability will be described here. Descriptions of the numerous other modifications will be found in Winkler's Chem. Unters. der Industrie-Gase ; Winkler and Lunge's Technical Gas Analysis ; and in Zeitsch. anal. Chem.

An extremely convenient device which is applied to almost all the forms of apparatus is the three-way stop-cock. This has the usual
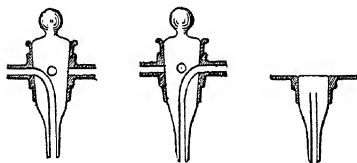
Fig. 38.

transverse bore, but the plug itself is elongated in the form of a tube, the bore of which is continued in a curved direction through the plug and opens at the side in the same plane, but in a direction at right angles to the transverse bore. By means of this tap two tubes can be made to communicate with one another, or either of them separately can be put in communication with a third tube or with the air.

Orsat's apparatus.—The measuring tube or burette consists of a cylindrical bulb terminating at one end in a capillary tube and at the other in a narrow tube of uniform bore graduated in tenths of a cubic centimetre. The total capacity of the tube from the zero to the capillary is 100 c.c., and the lower end of the tube is connected by caoutchouc tubing with a 'level-bottle,' the height of which can readily be adjusted. The burette is enclosed in a cylinder which is filled with water at a constant temperature. The capillary from the upper end of the measuring tube is carried horizontally along a wooden support. Other capillary tubes provided with stop-cocks are fused into it at right angles and communicate by means of very short lengths of stout indiarubber tubing with the absorption pipettes, each of which consists of a pair of

somewhat large cylindrical bulbs communicating at the bottom by a curved tube. The bulbs
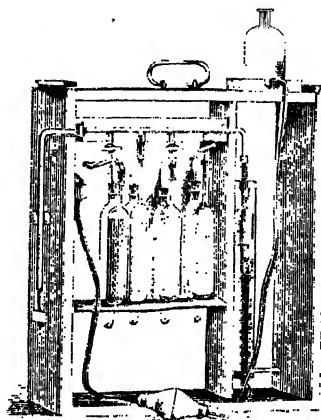
Fig. 39.

nearest the capillary tubes are fitted with short lengths of glass tubing so that a large surface of the reagent may be exposed, and the other bulbs receive the liquids when they are driven out from the first bulbs by the gas. Any number of bulbs can, of course, be attached to the main capillary, and at the end of it there is a three-way tap communicating with the aspirating tube or with the air.

The three absorption pipettes indicated in Fig. 39 are generally filled respectively with solutions of caustic potash, alkaline pyrogallate, and cuprous chloride, and serve for the estimation of carbon dioxide, oxygen, and carbon monoxide.

The burette is filled with water by placing the liquid in the level-bottle and raising the latter, and the stopcocks are then closed. The absorption bulbs are rather more than half filled with the liquid reagents, and by opening the stop-cocks and placing the level-bottle below the apparatus the liquids are drawn up so as to fill completely the bulbs connected with the capillaries. The stop-cocks are then closed.

The burette is filled with water up to the capillary tube by raising the level-bottle, and the far end of the capillary tube is connected with the tube along which the gas is to be conducted. The lower end of the three-way tap is connected with an indiarubber aspirator, and the air is removed from the conducting tube by aspirating the gas through it. The level-bottle is then lowered, the tap is turned through 90°, and the gas is drawn into the burette. When a sufficient volume has entered, the tap is closed, the levels inside and outside the burette are adjusted by raising the level-bottle, and the volume of the gas is read off as soon as the temperature is constant. If it is desired to operate upon exactly 100 c.c., the gas is drawn in until the water is a little below the zero, the tap is closed and the level-bottle is raised so that the gas is slightly compressed and the water rises

above the zero (time having been given for the liquid to run down from the sides of the burette), and the indiarubber tube is closed by a pinch-cock. The level-bottle is again lowered, and by cautiously opening the pinch-cock the water is allowed to descend exactly to the zero, and the pinch-cock is closed. The tap at the end of the main capillary is opened for an instant, so that the excess of gas may escape and the 100 c.c. remaining in the burette may be at atmospheric pressure.

In order to bring the gas into any one of the absorption bulbs, the level-bottle is raised and the tap of the particular bulb is opened. The gas passes into the bulb, and by alternately raising and lowering the level-bottle the gas can be passed backwards and forwards several times, care being taken that the absorbing liquid does not pass through the stop-cock. The gas is finally drawn off so that the absorbing liquid just reaches the stop-cock, the latter is closed, and, after readjusting the levels, the volume of gas is again read off. After making the necessary corrections, the decrease in volume is, of course, the volume of the gas which has been absorbed. The order in which the absorbing liquids should be applied has already been given (p. 236).

Lunge has added to this apparatus a capillary tube with palladium asbestos, for the estimation of hydrogen, connected with a bulb similar to the absorption bulbs, but containing water only. The apparatus also contains a small spirit-lamp carried by a movable rod for heating the palladium asbestos (Dingl. poly. J. 1882, 245, 512).

Sodeau has introduced a modification of Orsat's apparatus suitable for the analysis of mixtures containing only small proportions of combustible gases (*e.g.* chimney gases). In this modification the cuprous chloride pipette and the palladium combustion tube are replaced by a combustion pipette, the only absorption pipettes present being those containing caustic potash and alkaline pyrogallate. The carbon dioxide is first estimated by means of the former, and the combustible gases burnt by passing an electric current (5 amperes) for a short time through a platinum spiral in the combustion pipette. The contraction is noted, and the carbon dioxide produced is estimated by absorption in the caustic potash. These data give the proportions of carbon monoxide and hydrogen originally present in the gaseous mixture. The residual oxygen may now be estimated by absorption in the alkaline pyrogallate (Chem. News, 1904, 89, 61).

Bone and Wheeler's apparatus is a simple form of gas apparatus capable of giving accurate results with almost all gaseous mixtures ordinarily met with in technical practice. The working liquid is mercury, and the apparatus consists of the following parts : (1) A water-jacketed combination of measuring and pressure tubes, A and B, communicating through the glass tap C with the mercury reservoir D ; (2) an absorption vessel, F, standing over mercury in a mahogany trough ; (3) an explosion tube, E, fitted with firing wires, and having a separate mercury reservoir, H ; (4) a sampling tube, K. The connections between A, E, and F are of capillary bore throughout, with suitable glass taps

efore an analysis the whole of the apparatus, ncluding the connections, is filled with mercury,
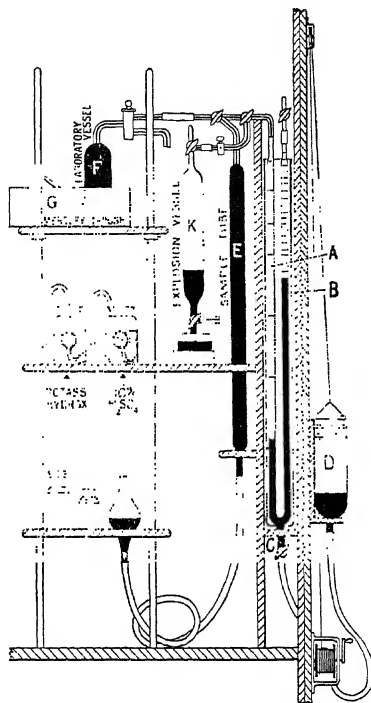
Fig. 40.

and the gas may be introduced either from the sampling tube, K, or from the absorption vessel, F.

The Regnault-Frankland principle of measurement is employed, namely, the measurement of the pressure of the gas (in mm. of mercury) at constant volume. The measuring tube A has a series of constant-volume marks coinciding with the 0. 100, 200, &c., mm. marks on the pressure tube B. These two tubes are moistened with dilute sulphuric acid (1 : 20) as a precaution against the accidental introduction of alkali into the measuring tube. The tap closing the upper end of the pressure tube is connected to it by stout indiarubber pressure tubing ; this gives a tight but elastic joint, and obviates risks of fracture. By means of this tap the pressure tube can be rendered vacuous, and, in this way, the measurements are rendered independent of the barometric pressure, and it becomes possible to analyse smaller volumes of gas. The length of the pressure tube provides for the requisite dilution of the explosive mixtures in analyses by explosion. All the absorptions are carried out in the same vessel, F, a comparatively small amount of freshly prepared reagent being used in each operation. The

absorption vessel is rinsed out by means of the three-way tap, the lower parallel limb of which is joined to a large bottle connected up with the water pump. In this way a series of absorptions can be carried out without disturbing a single connection in the apparatus. An analysis of producer gas is easily completed in 45 minutes, and one of coal gas requires about an hour (J. Soc. Chem. Ind. 1908, 27, 10). (For other forms of technical gas apparatus, v. F. Fischer, Zeitsch. angew. Chem. 1890, 3, 591; Sodeau, J. Soc. Chem. Ind. 1903, 22, 187. *See* also Chem. Soc. Trans. 1894, 65, 43; 1899, 75, 82; Ber. 1902, 35, 3485, 3493; 1907, 40, 4956; J. Soc. Chem. Ind. 1908, 27, 483, 491; Chem. Zeit. 1903, 845; 1904, 686; Zeitsch. angew. Chem. 1907, 20, 22.)

Hempel's apparatus.—The measuring apparatus consists of a burette, and a plain tube of the same length and diameter, which serves as a level-tube. The burette holds 100 c.c. from the zero to the capillary, is graduated in fifths of a c.c., and terminates at the top in a capillary tube to which is fitted a short piece of stout-walled caoutchouc tubing closed by a pinch-cock. Both the burette and the level-tube are fixed at the bottom into heavy circular stands, and each has a side tubulus near the bottom over which is slipped the caoutchouc tube by which they are connected. It is advisable to make all the joints secure with copper wire. In order to make the measurements more accurate, the burette may be surrounded by a wider tube filled with cold water (Winkler).

The pinch-cock is opened and both tubes are rather more than half filled with water. The burette is completely filled with water by raising the level-tube until the water runs out of the indiarubber tube at the top, and the pinch-cock is then closed. By means of the indiarubber tube the burette is attached to the conducting tube, which has already been filled with the gas, the level-tube is lowered, and the pinch-cock opened. When sufficient gas has been drawn in the pinch-cock is closed, the levels adjusted, and the volume read off in the usual manner. If it is desired to admit exactly 100 c.c., proceed in the same way as described under Orsat's apparatus.

The reagents are contained in absorption pipettes. Simple absorption pipettes consist of
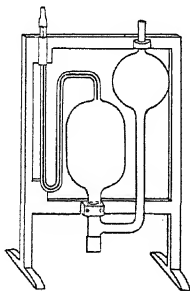
Fig. 41.

two bulbs which communicate at the bottom by a bent tube, one bulb being at a higher level than

the other (Fig. 34). The upper part of the lower bulb terminates in a straight capillary tube, which extends to a slightly greater height than the higher bulb, and serves to connect the pipette with the burette. In the tubulated pipette the bottom of the lower bulb is provided with a tubulus, which can be closed with a caoutchouc stopper, and through which solid reagents such
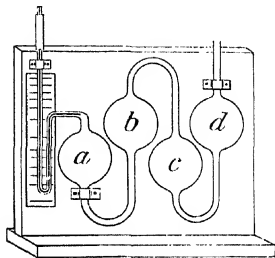
Fig. 42.

as phosphorus or zinc can be introduced. A composite absorption pipette consists of two similar pairs of bulbs, the second pair containing water or some other liquid which protects the reagent in the first from the action of the air. Composite pipettes are used with alkaline pyrogallate, cuprous chloride solution, bromine water, and similar reagents (Fig. 42).

In making the absorptions the pipettes, which are attached to wooden stands, are placed on a table stand of such height that the top of the capillary of the pipette is level with the top of the capillary of the burette. The burette and pipette are joined by means of short pieces of caoutchouc tubing and a short piece of capillary tube bent twice at right angles. The volume of air contained in this capillary is so small that it does not introduce any appreciable error. Care is taken that the capillary of the absorption pipette is filled just up to the top with the reagent. The connections being made, the level-tube, which should be full of water, is placed on the table stand and the pinch-cock is opened. The gas passes into the pipette, and by raising and lowering the level-tube the whole of the gas can be passed backwards and forwards two or three times; or the gas may be allowed to remain in contact with the liquid in the pipette. When absorption is complete, the level-tube is lowered until the reagent is drawn just up to the top of the capillary of the pipette, the pinch-cock is closed, and a second reading is taken.

When combustions of hydrogen or carbon monoxide have to be made, the capillary tube containing palladium asbestos is inserted between the burette and a simple absorption pipette containing water only. With gases containing both methane and hydrogen, the combustion is conveniently effected in an explosion pipette of spherical form, in which mercury is used as the working liquid. The two bulbs of the pipette are connected by thick-walled indiarubber tubing, and the explosion bulb can be closed by two stop-cocks.

When gases very soluble in water have to be measured, a burette is used, provided at the top with an ordinary stop-cock and at the bottom

with a three-way stop-cock, the volume between them being exactly 100 c.c. The burette must be perfectly dry before being filled, an end which is most quickly effected by rinsing the burette with water, then with alcohol, and finally with ether, and passing a current of warm
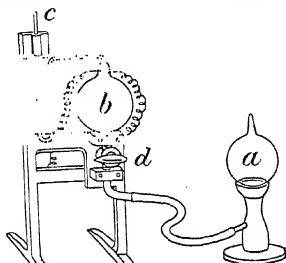
FIG. 43.

air through it. The lower end of the burette is connected with the conducting tube by means of the three-way tap d, the other end is connected with an aspirator, and a current of the gas is drawn through the burette until the air is completely expelled. The stop-cocks are then closed, care being taken that the gas in the tube is at
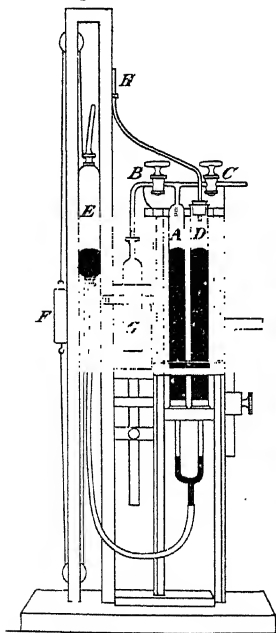
FIG. 44.

atmospheric pressure. The absorptions, &c., are made in the same way as with the ordinary burette.

Stead's apparatus consists (Fig. 44) of a graduated tube A, in which all measurements are made, fitted with taps B and C, leading respectively to the absorption vessel and the sampling tube. The lower end of A is joined by means of a T-piece to the mercury reservoir E, and to the tube D, which is open to the atmosphere at H. The readings are taken under atmospheric pressure. The gas sample is collected either directly in the laboratory vessel G or in Stead's sampling apparatus (Fig. 45). From either of these reservoirs a portion of the gas is introduced into the apparatus at C, and thence by opening B into the laboratory vessel G, which contains caustic potash solution standing over mercury. If the gas consists practically of carbon dioxide, carbon monoxide, and hydrogen, it is then
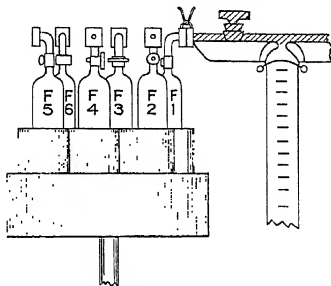
FIG. 46.

mixed with a known volume of oxygen, and the mixture sparked by means of platinum terminals fused into the upper part of the graduated tube A.

The contraction is ascertained and the carbon dioxide produced is estimated, and from these data the amounts of carbon monoxide and hydrogen are determined.

When other absorbable gases are present, then six absorption vessels are employed, and these are carried on a turn-table, so that each in turn can be brought into contact with the measuring tube (Fig. 46). In this modified form of the apparatus the eudiometer tube and each of the absorption vessels are fitted with a perfectly flat piece of plate glass perforated in the centre. These plates are lightly smeared with oil, and when communication is to be made between the eudiometer and the absorption vessel, these face plates are held together by a spring clip (Fig. 47).

FIG. 45.

FIG. 47.

A further improvement consists in the use of the modified form of absorption vessel shown
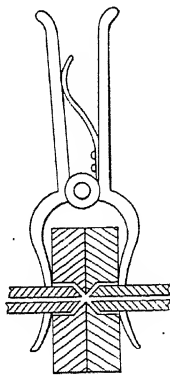
in Fig. 48, in which the reagent is contained in a glass bottle closed by an indiarubber bung
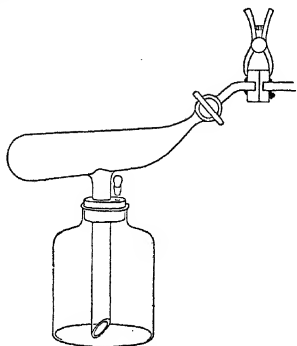
Fɪɢ. 48.

carrying a small glass stopper and a pipette furnished with a tap.

By means of these additions Stead's apparatus can be used for the complete analysis of furnace and producer gases and other technically important gaseous mixtures (J. Soc. Chem. Ind. 1889, 8, 178).

The nitrometer, originally devised by Lunge (Ber. 1878, 11, 436) for the estimation of nitrogen oxides in oil of vitriol, is capable of being applied to gas analysis and a large number of other determinations. It consists (Fig. 49) of a burette, fitted at the top with a three-way tap and a cup-shaped funnel, and communicating at

Fɪɢ. 49.   Fɪɢ. 50.
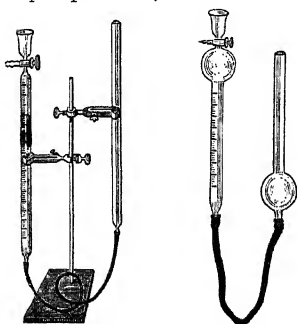
the bottom by means of caoutchouc tubing with a plain tube of the same diameter, which serves as a level-tube. When large quantities of gas have to be measured, the upper part of the burette is expanded into a bulb, and there is a similar bulb on the level-tube (Fig. 50).

This apparatus is used with mercury, and is thus suitable for the analysis of gases soluble in water. It can be used in the same way as Hempel's burette, and for all purposes to which the latter is applicable. It may also be used without absorption pipettes, the reagent being introduced by means of the cup, but since the reagents cannot be removed without

removing the gas, the latter method is only applicable when the reagents do not interfere with each other—*e.g.* for the absorption of carbon dioxide by caustic potash, followed by the absorption of oxygen by alkaline pyrogallate.

The estimation of nitrogen oxides in solution in sulphuric acid is conducted in the following manner. The apparatus is filled with mercury, so that when the tap is open between the burette and the cup, and the level-tube is raised, the mercury just passes through the tap and stands at a height of about 2 inches in the level-tube. The tap is then closed and 2–5 c.c. of the sulphuric acid, according to the quantity of nitrogen oxides which it contains, is placed in the cup, the level-tube is lowered and the tap is turned so that the acid is nearly all drawn into the burette without any air being admitted. To avoid measuring out small quantities (0·5–1 c.c.) of highly nitrated acid, this liquid should be diluted with a known volume of pure concentrated sulphuric acid, and 5 c.c. of this solution taken for analysis. The cup is rinsed with two successive quantities of 2–3 c.c. of pure acid, which is drawn into the cup with the same precaution as before. The tap being closed, the burette is taken out of the clamp and agitated in such a manner that the liquid is brought thoroughly into contact with the first 10 cm. or so of the mercury, which is broken up into bubbles. Nitric oxide is formed and collects in the upper part of the tube. When no more gas is given off, the levels are adjusted and the volume read off after the froth has subsided. In adjusting the levels the difference between the specific gravity of the acid and the mercury is allowed for by taking 6·5 mm. of acid = 1 mm. of mercury. A small quantity of acid is placed in the cup and the tap opened : if the acid is drawn in the pressure in the burette was too low; if gas escapes, the pressure was too high. It is better to err on the side of too low pressure, which is readily corrected by allowing acid to run in from the cup and taking another reading.

In agitating, care should be taken that the drop of acid which collects in the top of the burette just below the tap does not escape contact with the mercury, otherwise the results will be too low.

To prepare for another estimation, the level-tube is raised and the tap is opened so that all the acid and some of the mercury is driven into the cup, and the tap is then turned so that the acid runs out at the side.

The nitrometer may be used for the valuation of nitrites and nitrates, which are introduced in the form of a concentrated aqueous solution, care being taken that the proportion of water to acid does not exceed 2 parts of aqueous solution to 3 parts of the strongest acid. It may also be used for the estimation of nitrates and nitrites in potable waters, and in fact for almost any determinations in which a definite volume of gas is given off. For example, the estimation of carbonic acid ; of urea by hypobromite (the reading being increased by 9 p.c. to correct for solubility of the gas and incomplete decomposition) ; hydrogen peroxide by an acidified solution of potassium permanganate, or, *vice versa*, the value of a permanganate solution by means of hydrogen peroxide, &c. (*See* Lunge,

Ber. 1878, 11, 436 ; J. Soc. Chem. Ind. 1885, 4, 447, and 1886, 5, 82 ; Zeitsch. anal. Chem. 25, 309 ; and the translation of Winkler's Technical Gas Analysis (1885); also Allen, J. Soc. Chem. Ind. 1885, 4, 178.)

The *gas-volumeter*. Several of the estimations referred to in the preceding paragraph are more conveniently carried out in the gas-volumeter devised by Lunge, as in this apparatus the decomposition can be effected in a separate vessel. The measuring tube A and the reservoir C are converted by means of the T-piece D, with the so-called 'reduction' tube B.

FIG. 51.

At the outset the temperature and pressure are observed, and the volume occupied under these conditions by 100 c.c. of dry (or moist) air measured at 0° and 760 mm. is calculated. The reduction tube is filled with air to this volume, and the tap of the tube closed, or the end of the reduction tube may be terminated by a capillary and sealed off after the volume has been correctly adjusted. A special tap for the reduction tube has been devised by Göckel (Zeitsch. angew. Chem. 1900, 13, 961, 1238). If moist gases are to be measured, a small drop of water is introduced into the reduction tube ; if dry gases are under examination, a drop of concentrated sulphuric acid must be introduced into the reduction tube. The formulæ for calculating the volume of gas in the reduction tube are as follows :—

$$V_1 \text{ (dry gases)} = \frac{V_0(273+t)760}{273 \times B}$$

$$V_1 \text{ (moist gases)} = \frac{V_0(273+t)760}{273(B-f)}$$

where V_1 = volume of gas required ;
V_0 = normal volume (*e.g.* 100 c.c.) ;
t = observed temperature ;
B = observed barometric pressure ;
f = tension of water vapour at observed temperature.

When a decomposition by sodium hypobromite or hydrogen peroxide has been carried out in the auxiliary generating bottle, the gas evolved passes into the measuring tube A. The mercury in A and C are then adjusted to the same level, and the tap o closed, the gas being then at the atmosphere pressure. The three tubes are now adjusted so that the mercury in A and B are at the same level when the mercury in the latter tube stands at the 100 c.c. graduation. The gases in A and B are at the same

temperature and under the same pressure, and since the gas in B occupies the same volume as it would at 0° and 760 mm. pressure, it follows that the gas in A also occupies the same volume as it would under the standard conditions. In this way, by the use of the gas-volumeter, all thermometric and barometric readings and all reductions by calculations or special tables are avoided ; for the volume of gas is read off directly under conditions corresponding to the normal pressure and temperature. It is, however, essential that the reduction tube should be arranged for dry or moist gases according to the nature of the analytical operation involved (*v.* Lunge, Ber. 1890, 23, 440; 1891, 24, 729 ; 1892, 25, 3157 ; Zeitsch. angew. Chem. 1890, 3, 129 ; 1891, 4, 197, 410 ; 1892, 5, 677 ; J. Soc. Chem. Ind. 1890, 9, 547. *Cf.* Gruskiewicz, Zeitsch. anal. Chem. 1904, 43, 85).

In addition to the hypobromite and hydrogen peroxide decompositions, Lunge and Marchlewski have adapted the gas-volumeter to the estimation of carbon dioxide in natural carbonates, Portland cement, and other mineral substances, and also to the determination of carbon in iron and steel (Zeitsch. angew. Chem. 1891, 4, 229 ; 1893, 6, 395 ; J. Soc. Chem. Ind. 1891, 10, 658).   G. T. M.

ELECTROCHEMICAL ANALYSIS.

The first suggestion to apply the electric current to the deposition of metals was made by Cruickshank in 1801 (Nicholson's Journal of Nat. Phil. 1801, 4, 254). He noticed that metals were deposited from acid or alkaline solutions of their salts at the negative pole, and that the metal went into solution at the positive pole. He therefore suggested that the electric current might thus be used as an aid to analysis, particularly for depositing lead, copper, and silver.

In 1812 Fischer suggested its use for detecting small quantities of arsenic (Gilbert's Annalen, 42, 92). In 1840 Cozzi (Arch. delle Science med. fis 50, ii. 208) employed the galvanic current (produced by plates of gold and zinc connected together by a wire) to ascertain whether organic fluids, such as milk, contained metallic impurities. Gaultier de Claubry (J. Pharm. Chim. iii. 17, 125) applied it to detect small quantities of arsenic in animal fluids. In 1861, Bloxam (Quart. Journ. Chem. Soc. 13, 12, 338) described an electrolytic method for detecting arsenic and antimony. Becquerel (Ann. Chim. Phys. 1830, 43, 380) found that manganese and lead were readily oxidised, and appeared as oxides on the anode.

All these workers appear to have merely used the electric current as an aid to qualitative analysis. Wolcott Gibbs (Zeitsch. Anal. Chem. 3, 334), in 1864, showed that copper, nickel, zinc, lead, and manganese might be quantitatively determined by means of the electric current. Lucknow (Dingl. Poly. J. 1865, 177, 231, and 178, 42), from 1860, had employed electrolytic methods for the quantitative analysis of copper salts and for commercial copper. From this time forward many workers entered the field, and about 1880 Edgar Smith in America, and Classen in Germany, very much advanced the subject of electro-analysis, and to-day it is one of the most useful helps to the analytical chemist.

Before dealing with the methods of deposition and separation of the metals, it will be well to describe the apparatus used; but only the apparatus most generally employed will be dealt with.

Classen first suggested the employment of a platinum basin as cathode and a platinum disc as anode. A convenient stand for holding the basin, and a method of connecting with the source of current, are shown in Fig. 52. The basin should hold from 150 to 180 c.c. of solution. The inner surface of the basin should be roughened by the sand blast, as this causes better adherence of the deposit, especially in the case of peroxides such as lead and manganese. The base of the stand is of slate or marble, and the brass rod which conveys the — current is hollow; through this brass rod an insulated wire for carrying the + current passes, and is connected at the top of the rod by means of a piece of ebonite.
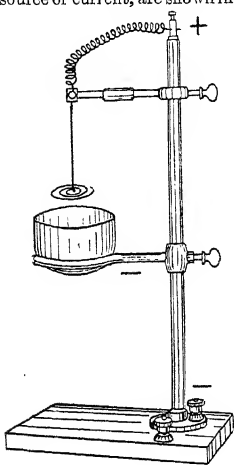
Fig. 52.

The ring which supports the basin has three little platinum points at equal intervals on its circumference; on these the basin rests, thus ensuring good contact. The positive pole of the source of current is connected with the binding-screw fixed to the slate base, and the negative pole with the binding-screw marked —.

Another useful form of electrode is illustrated in Fig. 53. The anode is a stout spiral of platinum and the cathode is a cylinder of platinum gauze. This form of electrode can be employed either for stationary work or for rapid deposition work when the anode is rotated. The vessel in which the electrolysis takes place may either be a beaker, or, better, a funnel with a tap such as is illustrated in Fig. 67.

Fig. 53.

For stationary work the Flag electrode of F. Mollwo Perkin (Fig. 54) gives very satisfactory results. The cathode consists of a small sheet of stout platinum gauze, autogenously fastened on to a rigid platinum-iridium frame, both frame and gauze being roughened by the sand blast. The wire holds the electrode in position during the analysis. The loop near the top of the wire serves to hang the electrode on the balance. The anode is made of platinum wire, and is bent upon itself in such a way that when it is placed in position for electrolysis, as illustrated in Fig. 55, an even density is obtained on all parts of the cathode.

It has been found that the rate of deposition of metals from their solutions is very much increased and higher current densities can be employed when either the anode or cathode is rapidly rotated. Frary

Fig. 54.
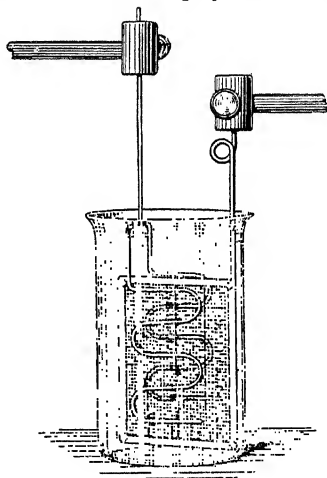
Fig. 55.

(Zeit. f. Elektrochem. 1907, 308) has also shown that excellent results can be obtained by electrolysing with stationary electrodes, but causing agitation of the electrolyte by placing the whole apparatus in the field of a powerful electro-magnet. The forms of the apparatus are depicted in Fig. 56. From the figure it is seen that the solution is contained
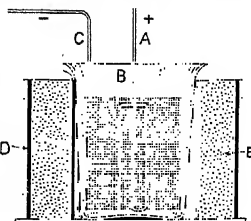
Fig. 56.

in a beaker B, in which is a cylindrical platinum gauze cathode C and a heavy platinum wire as anode A. The beaker is placed in the centre of a spool made from insulated copper wire E. By passing an electric current through the copper wire of the spool, a powerful magnetic field is produced, in the centre of which the beaker stands. If now a current be passed through the electrolyte by means of the electrodes, the electric lines of force are cut at right angles by the magnetic lines of force, and this produces a tendency for the solution to rotate, owing to the vertical magnetic field and radial current lines. The speed of rotation depends upon the ratio between the electric current and the magnetic current. With an electrolysing current of from 6 to 7 amperes, Frary was able to deposit 0·850 gram copper in 15 minutes. The other form, illustrated in Fig. 57, is for electrolysing with a mercury cathode, the use and applications of which will be described later. The electrolysing vessel is ring-shaped, so that it may fit into a hole cut into the pole D of the magnet. An iron rod passes from the other pole up into the centre of the electrolysing vessel. A is the anode and C the cathode. Extremely rapid rotation is thus
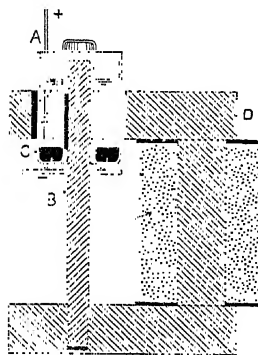
FIG. 57.

produced, because the iron core very much facilitates the passage of the magnetic current, there being a radial field with vertical current lines.

The advantages claimed for this method are : rapidity of deposition, and, as there are no mechanical parts which require lubrication, there is no chance of contamination from oil or grease accidentally falling into the solution. As a matter of fact, however, rapid methods of electrolysis are more frequently carried out by means of a rotating anode or cathode.

Gooch and Medway (Amer. J. Sci. 15, 320) use a rotating cathode. It is made from a platinum crucible of about 20 c.c. capacity. The crucible is attached to the shaft of the electromotor, which is used to rotate it at a speed of from 600 to 800 revolutions per minute by fitting it over a rubber stopper with a central bore, into which the end of the shaft fits tightly. In order to make electrical connection between the crucible and the shaft of the motor, a narrow strip of sheet platinum is soldered to the shaft and bent upwards along the sides of the stopper. This connects the shaft with the inside of the crucible when the latter is pressed over the stopper. The anode consists of a half cylinder of sheet platinum.

Fig. 58 represents the arrangement of the apparatus when fitted together.
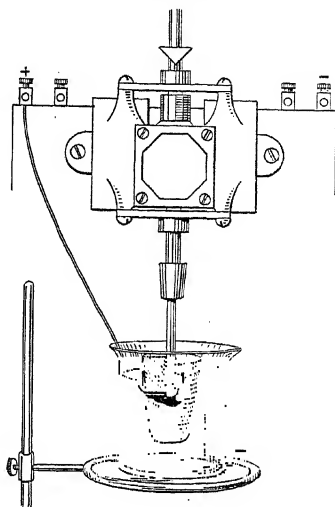
FIG. 58.

F. Mollwo Perkin and W. E. Hughes (Trans. Faraday Soc. 1910, 14) use an electrode of sheet platinum spun up so as to form a narrow thimble (Fig. 59), the upper end being open and having a stout iridio-platinum wire fused on to it by means of three short wire supports. This electrode is fixed into a small chuck and rapidly rotated by means of an electromotor, the speed of rotation usually being from 750 to 950 revolutions per minute. When in use, about two-thirds of the length of the thimble is dipped into the electrolyte, the active surface being about 16·3 sq. cm. If dipped too deeply into the solution, there is a tendency for the liquid to splash into the interior of the cylinder, and this would, of course, lead to erroneous results. The anode consists of a platinum cylinder of fine mesh. It is, however, frequently more satisfactory to employ a rotating anode and a stationary cathode, and for this purpose the gauze anode is employed as cathode, and the anode consists of a spiral of stout iridio-platinum wire. The simplest arrangement is illustrated in Fig. 53. The electrolysing vessel consists of a tap funnel which, when the electrodes are covered, holds about 60 to 70 c.c. of solution. The advantage of this form of electrolysing vessel is the ease with which the electrolyte can be removed on the completion of the electrolysis and the electrodes washed. The method of procedure is to place a beaker beneath the tap and draw off the solution until about half of it has run in. Distilled water is then run up to the original mark and the solution drawn off as before. The operation is repeated until the ammeter needle sinks to zero. The remaining water is

FIG. 59.

run off, the tap closed, and the funnel filled with pure methylated spirit. This is run off, and,

Fig. 60.

after a final washing with absolute alcohol, carried out in the same manner, the electrodes are removed and the cathode dried in the steam oven.

Another form of rotating cathode devised by Perkin is illustrated in Fig. 60. The cathode consists of a cylinder of platinum gauze. The anode is in the form of a double circle of stout platinum wire, and has four small baffle plates so placed as to prevent it from rotating with the cathode.
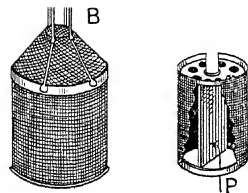
In order to rotate the anode (or cathode), it is fixed into a small chuck fastened on to the end of the spindle of a bicycle hub. The barrel of the hub has an arm fastened into it which can be clamped to any suitable support. The upper end of the spindle has a sheaf of pulleys fastened to it, so that it can be rotated by means of a belt from a motor and different speeds be obtained. It is found that the current passes very well through the barrel of the hub and the balls, which are lubricated with oil and graphite, to the spindle, and so to the electrode. When it is desired to obviate all drop in potential, e.g. if the apparatus is to be used for graded potentials,

Fig. 61.

then a mercury cup is fastened on to the top of the spindle so that the current passes directly to the spindle.

The apparatus of H. J. Sand (Trans. Chem. Soc. 1907, xvi. i. 373) is rather more complicated, but gives equally satisfactory results.

The special object in the design of this electrode was to produce an apparatus which could be satisfactorily employed for the separation of metals by graded potentials. It consists of a pair of platinum gauze

Fig. 62.

electrodes (Fig. 61), an inner rotating electrode A, and an outer electrode B. The two are kept in position relatively to each other by means of a glass tube, which is slipped through the collar and the ring of the outer electrode B. It is gripped firmly by the former, but passes loosely through the latter. The hollow iridio-platinum stem A of the inner electrode is passed through the glass tube, in which it rotates freely. The mesh of the gauze is 14^2 per sq. cm. The gauze of the outer electrode almost completely stops the rotation of the liquid. The electrolyte is, therefore, ejected rapidly from the centre of the inner electrode by centrifugal force, and is continually replaced by liquid drawn in from the top and the bottom. So great is the suction thus produced, that when the electrode is moving rapidly, chips of wood or paper placed in the solution are drawn down to the top of the outer electrode. The circulation is practically independent of the size of the beaker employed. As the outer electrode surrounds the inner completely, the lines of flow of the current are contained between the two, and even when strong currents are employed, the potential

of the electrolyte anywhere outside the outer electrode is practically the same as that of the layer of liquid in immediate contact with it. Fig. 62 shows the apparatus with stand and motor in working order. Before the method adopted for electrolysing by means of graded potential is discussed, the mercury cathode devised by Smith and Howard will be described.

Wolcott Gibbs, in 1880, first suggested the use of metallic mercury as cathode, a definite amount being weighed into a beaker, where it was connected by means of platinum wire with the negative pole of a battery. Various metallic salt solutions were experimented upon, and, in 1883 (Amer. Chem. J.13,571), Gibbs stated
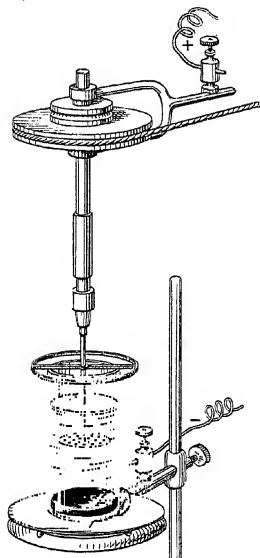
FIG. 63.

that ' It was found possible to separate iron, cobalt, nickel, zinc, cadmium, and copper so completely from solutions of the respective sulphates that no trace of metal could be detected in the respective liquids.' Gibbs had in view not only the determination of the metals, but also of the anion left in the solution by titration.

In 1886 Luckow (Chem. Zeit. 9, 338, and Zeitsch. anal. Chem. 25, 113) suggested the addition of a known weight of a solution of a mercury salt to a solution of zinc sulphate, and so to deposit zinc and mercury simultaneously. In 1891 Vortman (Ber. 24, 2749) suggested a similar method, and employed it in the determination of several metals. Drown and McKenna (Amer. Chem. J. 5, 627) further worked at the subject, using an apparatus somewhat similar to Wolcott Gibbs, that is to say, an actual mercury cathode, but the process was first successfully worked out by Edgar Smith and his collaborators (J. Amer. Chem. Soc. 25, 885). The apparatus employed consists of a small tube or beaker of about 50 c.c. capacity, close to the bottom of which a thin platinum wire is introduced by means of which the current is supplied to the mercury cathode (Fig. 63).

The external part of the platinum wire touches a disc of sheet copper on which the beaker rests, and which is connected with the negative source of the current.

The anode is either a perforated disc of platinum or a stout spiral of platinum wire. During the electrolysis the anode is rapidly rotated by means of an electromotor or water turbine.

The chief difficulty in using the mercury cathode is the trouble experienced in washing and drying it. The solution left at the end of the electrolysis is siphoned off, and at the same time distilled water is run in until the needle of the ammeter drops to zero. Then, and not till then, the current is switched off. The inside of the beaker and the amalgam are rinsed with alcohol three times, and finally with dry ether. It is advantageous, in order to drive out thoroughly the last traces of ether, to blow dry air into the beaker for a few minutes. After standing for half an hour, the apparatus is ready for weighing. F. M. Perkin (Trans. Faraday Soc. 1910, 14) uses a small quartz beaker as containing vessel, with an iridium wire fused into it to make contact with the mercury. The advantage of iridium is that it does not amalgamate with the mercury. An advantage of the quartz vessel is that it can be heated to redness for purposes of cleansing. The apparatus is illustrated in Fig. 64. It will be noticed that a siphon tube is fused into one side of the beaker. The layer of mercury must not be sufficient in quantity to close the side tube. A spiral iridio-platinum anode is employed. When the electrolysis is finished, a piece of rubber tube is fastened to the bent end of the siphon. Distilled water is added so that the solution begins to siphon over into a beaker placed below the rubber tube. In order to work with

FIG. 64.

as small a quantity of water as possible and in cases where the solution is required again, e.g. in metal separations, the solution is allowed to run out until its level drops almost to the end of the anode. Fresh water is then run in, and the operation repeated until the ammeter needle points to zero. For purposes of steadiness the vessel is held between clips on a copper plate.

By means of the mercury cathode not only can the cations be rapidly and accurately determined, but also the anions remaining in the solution.

Method of Graded Potential.

Each metal has a particular potential at which it begins to be deposited; below this potential it is not possible to deposit the metal. It follows, therefore, that when dealing with a solution containing the salts of two or more metals it will be possible, provided the deposition potentials of the metals do not lie too near together, to deposit separately the metals, by first working with the lowest potential when one of the metals will be deposited. When this metal has been deposited the next one in the potential series will be deposited if the potential is raised.

This method of analysis was suggested by Kiliani in 1883, and was further elaborated by
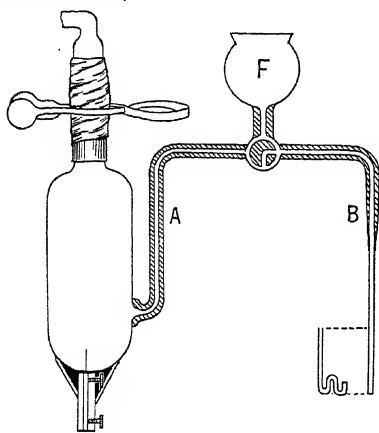
FIG. 65.

Freudenberg working in Ostwald's laboratory (Zeit. physikal. Chem. 12, 97). But it was
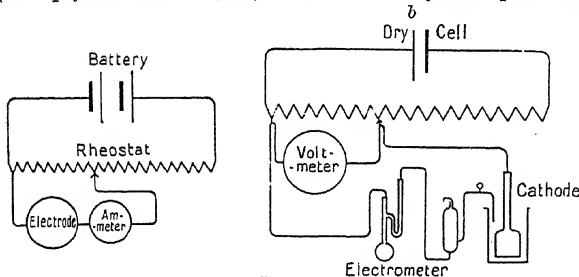
FIG. 66.

H. J. S. Sand (Trans. Chem. Soc. 1907, 373) who first worked out the method and used the apparatus with the rotating cathode already mentioned. The potential is kept at constant value by means of an *auxiliary electrode*. Such an auxiliary electrode, designed by Sand, is illustrated in Fig. 65. It is a mercury-mercurous sulphate 2N-sulphuric acid electrode. The distinctive feature of the electrode is in the funnel F, and connecting glass tube AB. The two-way tap allows the funnel F to be connected with either limb of the glass tube AB, or closes all parts from each other. The limb A permanently contains the 2N-sulphuric acid solution of the electrode. But the limb B is filled for each experiment from the funnel F with a suitable connecting liquid, generally sodium sulphate solution. The end of B is made of thin tube

FIG. 67.

of about 1½ mm. bore, and is bent round several times to minimise convection. While the electrode is in use, the tap, which must be kept free from grease, is closed, the film of liquid held round the barrel by capillary attraction, making the electrical connection, but towards the end of a determination, a few drops are run out in order to expel any salt which may have diffused into the tube.

Electrical connections.—For separations by graded potential the electrical connections must be made as shown in Fig. 66 *a* and *b*. The battery is connected directly to the two ends of a sliding rheostat, the electrolytic cell to one of them and the slider. It is essential that the sliding contact should be good. The arrangement adopted for the measurement of the potential-difference auxiliary electrode-cathode is one which has been frequently employed in electro-chemical research. The electromotive force to be measured is balanced against a known electromotive force by means of a capillary electrometer. The known electromotive force is drawn from a sliding rheostat, the ends of which are connected with one or two dry cells. The value of the E.M.F. is read directly on a delicate voltmeter (range 1·5 volts). For potential differences greater than 1·5 volts, a Helmholtz 1-volt instrument may be interposed between the auxiliary electrode and the rheostat. The arrangement allows the voltage to be measured almost instantaneously, which is a matter of great importance.

To carry out an experiment, the cathode, anode, and auxiliary electrode are placed in position, the electrolyte is heated to the required temperature, and covered with a set of clock-glasses having suitable openings for the electrodes. For the purpose of a separation, the current is usually started at about 3–4 amperes, and the potential of the auxiliary electrode noted. As a rule, this is only slightly above the equilibrium potential. The current is then regulated so that the potential of the electrode may remain constant. When no side-reactions take place, the current falls to a small residual value (generally about 0·2 ampere), as the metal to be separated disappears from the solution. The auxiliary electrode is then allowed to rise 0·1–0·2 volt, according to the metal.

It is obviously a matter of great importance to know when all the metal has been deposited. Under the conditions just assumed, the amount deposited per unit of time may be taken as roughly proportional to the amount still in solution. This being so, it follows that the amount in solution will decrease in geometrical ratio during successive equal intervals of time. If we, therefore, make the safe assumption that the concentration of the metal has fallen to under 1 p.c. of its original value in the time during which the potential and the current have been brought to their final value, it is clear that by continuing the experiment half as long
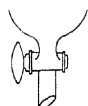
again, the concentration of the metal will fall to under 0·1 p.c., so that the deposition can be considered finished.

In cases where side-reactions occur, the current does not fall to zero, but it generally attains a constant value which allows it to be seen when all the metal has been removed. In certain cases this can be tested for chemically, and by continuing the experiment for about half as long again as this reaction demands, the metal may be safely assumed to have been deposited completely. This method may be adopted, for example, in the separation of lead from cadmium, the former being roughly tested for by sulphuric acid. If none of these methods is available, the metal must be deposited to constant weight, or else the separation must be carried out under very carefully defined conditions for a length of time proved by previous experiment to be more than sufficient.

Sand has simplified the apparatus necessary for the potential measurements by fitting all the apparatus required for the measurement of the electrode potential into a single box. Full particulars will be found in Trans. Faraday Soc. 1909, 162.

F. M. Perkin uses the apparatus depicted on p. 248 for working with graded potentials. The vessel containing the electrolyte has a tube fused into the side. Into this side tube the capillary end of the auxiliary electrode is inserted (Fig. 67).

CLASSIFICATION OF THE METALS FOR ELECTRO-ANALYTICAL PURPOSES.

Most metals can be deposited satisfactorily at the cathode, particularly since the introduction of the mercury cathode and of the graded potential methods. Theoretically, by grading the potential, it should be possible to separate any one metal from another. Indeed, in many cases, this can be done, but there are cases in which the potential differences at which two metals can be deposited, that is to say, the minimum potential at which they will both be deposited, lie so close together that it is not possible to so adjust the conditions that a separation can be effected.

GROUP I.—Copper, silver, mercury, gold, palladium, rhodium, platinum, iridium, bismuth, antimony, tin, (arsenic), tellurium. These metals are more electronegative than the hydrogen electrode, and, consequently, can theoretically be deposited quantitatively from acid solutions.

GROUP II.—Cadmium, zinc, and indium. These metals are more electropositive than hydrogen, but, owing to the supertension of the hydrogen evolution in acid solution, it is actually possible to deposit them from weak acid solutions.

GROUP III.—Iron, nickel, cobalt. These metals are more electropositive than hydrogen, but, as the supertension of hydrogen is very low, these metals cannot be deposited completely from acid solutions. They can, however, be deposited from acid solutions if a mercury cathode is employed.

GROUP IV.—The metals of this group can either be deposited as oxides at the anode, or as oxides at the cathode. The group comprises the following metals : lead, thallium, manganese, chromium, molybdenum, uranium. Some of them can, however, be satisfactorily deposited as an amalgam on a mercury cathode.

GROUP V.—The metals of this group are the most strongly electropositive, and can only be deposited by using a cathode of mercury ; but even then it is not possible in all cases to obtain a quantitative separation. The metals of this group are aluminium, glucinum, calcium, strontium, barium, magnesium, potassium, sodium, lithium, rubidium, cæsium.

GROUP VI.—These are all anions, and their estimation has been rendered possible mainly through the work of Edgar Smith, who completely deposits the metals by means of a mercury cathode and estimates the anions by titration or other appropriate method. The most important anions analysed by this method are F', Cl', Br', I', SO_4'', CO_3'', $Fe(CN)_6''''$, $Fe(CN)_3'''$, PO_4''', NO_3'.

It has not been found possible to analyse organic anions by electrolytic methods, because they are either decomposed or various reactions more or less complicated take place. Thus, for example, when the acetate anion is given up at the anode, ethane is produced, which, of course, is given off in the form of a gas.

Nature of Deposit.

Sand (Trans. Chem. Soc. 1907, 383) has theoretically and practically worked out the conditions necessary for obtaining adherent metal deposits.

The production of a *uniform deposit* over the electrode depends entirely upon the relation between polarisation and the E.M.F. required according to Ohm's law to force the current from one part of the solution to the other (Zeitsch. Elektrochem. 1904, 452). The case of metals such as cadmium and zinc, which require a higher potential for their precipitation from most of their solutions than hydrogen, is a question of supertension. The metals can only be deposited by virtue of the supertension which is required to liberate hydrogen as a gas. This supertension varies with the material of the electrode, and may even vary at different parts of the same electrode, owing to different states of its surface. Consequently, it may happen that the metal is deposited on a portion of the electrode which has a high supertension, and will continue to grow there ; but at rougher parts of the electrode, where the supertension is lower, hydrogen alone will be evolved. This is, for example, particularly noticeable in the case of zinc, which, instead of being evenly deposited over the surface of an electrode, apparently perfectly smooth and even, often comes out in patches, parts of the electrode being absolutely free from deposit. Some solutions also of the same metal appear to be more sensitive to variations in the quality and character of the electrode than others. Thus with ordinary electrodes when the potential is not graded, it is a matter of the greatest difficulty to obtain an adherent deposit of copper when the electrolyte is sulphuric acid. On the other hand, with electrolytes of potassium cyanide or nitric acid, an even deposit is readily produced.

The nature of the deposit.—Electrolytic deposits may be spongy, coarsely crystalline, or

finely crystalline. The last is the only form in which metals may be deposited in order to yield satisfactory quantitative results. Sand considers (*l.c.*) that spongy deposits are most probably due to the metal being deposited in the form of an unstable hydride, which gradually decomposes with evolution of gas.

The difficulty of hydride formation is got over by keeping the potential of the electrode under control. Vigorous stirring of the electrolyte, small current density, and the presence of some oxidising agent, tend to keep the potential low. But, by using an auxiliary electrode and rapid rotation, it is possible to obtain metals from solutions from which, under ordinary circumstances, they cannot be deposited.

Copper.

Copper may readily be deposited from solutions which contain considerable quantities of nitric or sulphuric acid. But good deposits can also be obtained from cyanide solutions, and it is possible to employ solutions containing an excess of ammonia.

The solutions which give the best results are those containing nitric acid or potassium cyanide. Indeed, it is a matter of considerable difficulty to obtain satisfactory results in presence of free sulphuric acid, excepting when a mercury cathode is employed. For stationary work, either the gauze flag electrode or the cylindrical gauze electrode is to be recommended.

Nitric acid.—About 1 gram of the copper salt is dissolved in about 140 c.c. of water, and 5–10 c.c. of nitric acid (sp.gr. 1·42) added to the solution ; that is, from 8 to 10 p.c. of the acid. If the flag electrode is employed, usually about 120 c.c. of water is sufficient, in which case proportionately less nitric acid must be used. The solution may either be electrolysed at ordinary atmospheric temperature, or heated from 45°–50° ; in the latter case the time required for the complete deposition of the metal is considerably lessened. The best C.D. to employ is from 0·8 to 1·2 amperes, when the E.M.F. will be from 1 to 2·8 volts. A bright red film will be seen to flash across the cathode almost immediately the circuit is completed. In cold solutions, from 2½ to 3 hours will be required to completely deposit the metal ; with hot solutions the rate of deposition is considerably accelerated. To ascertain when the whole of the copper has been deposited, withdraw about 1 c.c. of the solution by means of a pipette, transfer to a test-tube, make alkaline with ammonia, then acid with acetic acid, and add a few drops of potassium ferrocyanide : the formation of a brown precipitate or colouration shows that there is still some copper left in the solution, in which case, of course, it is necessary to continue the electrolysis until, on further testing with the reagent, no colouration is produced.

Washing the deposit.—As the electrolyte contains an excess of free nitric acid in which the copper deposit is readily soluble, the washing has to be carried out with caution. Some workers prefer to siphon off the electrolyte without breaking the circuit, and to run in water at the same time, until the ammeter points to zero. The current is then cut off and the cathode removed, finally washed with distilled water and

dipped into a beaker of absolute alcohol. It is then dried in the steam oven, and, after cooling for 20 minutes, weighed. When the gauze cylindrical electrode is used, a stoppered funnel as illustrated in Fig. 67 is very convenient.

The solution is drawn off until only about one quarter of the electrode is immersed. Distilled water is then run in, and the operations repeated until the ammeter shows zero. By operating rapidly, the cathode may be removed, and, if dipped at once into a beaker of water and then washed under the tap or in several changes of water and then in alcohol, absolutely accurate results can be obtained.

The deposit obtained from nitric acid is bright red, and generally has a more or less crystalline appearance. If the C.D. has been too high, it may be ' burnt,' and have a brownish appearance, and may be powdery and nonadherent. When it is desired to electrolyse over-night—and this is often found very convenient—a C.D. of from 0·2 to 0·3 of an ampere is used. It is generally advisable in this case to add more nitric acid, because, owing to the reducing action of the hydrogen liberated at the cathode, the nitric acid becomes converted into ammonia. This formation of ammonia causes the deposit to be spongy and of a bad colour, when it is difficult to wash and weigh. For running over-night about 2 c.c. extra of nitric acid should be added for every 100 c.c. of solution.

The deposits obtained with sulphuric acid are generally not satisfactory, but of all the copper deposits that obtained from solutions containing potassium cyanide is the most beautiful.

Potassium cyanide.—The colour of the deposited metal is pinkish red, and perfectly smooth. But, from other points of view, the deposition from cyanide solutions has no advantage over the deposits obtained from solutions containing nitric acid. The copper salt is dissolved in about 30 or 40 c.c. of distilled water, and then a freshly prepared solution of potassium cyanide added, until the precipitate first produced is dissolved. Slightly more potassium cyanide than is necessary to dissolve the precipitate should be used, but any considerable excess must be avoided. Generally speaking, from 1 to 1·5 grams of potassium cyanide should be used for every gram of copper salt taken.

The C.D. employed should be from 0·8 to 1·2 amperes. The E.M.F. required in cold solutions will be found to be about 5–6 volts ; in warm solutions, from 4 to 5 volts. The whole of the copper is deposited in 2 to 2½ hours.

Rapid methods.—By employing rotating electrodes, either rotating anode or cathode, copper may be completely deposited in a few minutes. Thus Sand, by using his apparatus, was able to completely deposit the copper from 0·25 gram copper sulphate in 6 minutes, the number of revolutions of the anode per minute being about 800 ; in that of Fischer the copper from 0·3 gram copper sulphate was deposited in 10 minutes, the speed of revolution being 1000 to 1200. In the one case a rotating anode was employed and in the other the cathode was rotated. The electrolyte in both cases contained free nitric acid. Cyanide solutions give, however, equally satisfactory results.

Edgar Smith, by employing a rotating anode and mercury cathode, has deposited quantitatively 0·789 gram of copper in 10 minutes, and as much as 0·3945 gram per 4 minutes, the solutions containing sulphuric acid. The advantage of the mercury cathode is that almost any electrolyte can be employed equally satisfactorily. Indeed, the pure salt of the metal may be dissolved in water and electrolysed without the addition of any acid or other electrolyte. When the whole of the metal has been deposited, the solution is run off, and may then be titrated in order to determine the anion, e.g. SO₄″ (p. 247).

Silver.

Silver can best be deposited from solutions containing potassium cyanide. From solutions containing other electrolytes it is apt to be deposited in a crystalline feathery form, and consequently does not adhere well to the cathode. There is, however, a tendency for the results to be slightly too low when cyanide solutions are employed. It is very important that only the purest potassium cyanide be used in making up the solutions. For 0·5 gram of a silver salt about 3–4 grams of potassium cyanide will usually be found sufficient. With a C.D. of 0·5 to 1·0 ampere, and a temperature of 50°–60°, the silver will be deposited in from 1 to 2 hours. Using a cold solution and with a C.D. of from 0·2 to 0·35 ampere, the time required is from 4 to 4·5 hours. The deposit should either be washed by siphoning, or the electrode must be very rapidly removed from the electrolyte and dipped into water, in order to avoid loss by the solvent action of the potassium cyanide.

With rotating electrodes the silver can be deposited within a few minutes. By using an auxiliary electrode and rotating the anode vigorously, Sand was able to deposit silver from ammoniacal solutions in 7 to 8 minutes.

Smith, by using a mercury cathode and rapidly rotating anode deposited 0·2240 gram of silver from silver nitrate in 4 minutes. At the commencement of the operation an anodic deposit of silver peroxide was obtained, but after a minute or two this disappeared.

Mercury.

Many methods have been devised for precipitating mercury on platinum cathodes, and some of them give quite satisfactory results. When mercury is deposited on a platinum dish, or on a wire gauze electrode, it spreads evenly over the surface as a thin metallic film, which, however, is inclined to run together as the amount of mercury on the electrode increases in quantity. After the mercury has been deposited, the electrode is washed with water in the usual way, then in absolute alcohol, and finally in absolute ether. The last traces of ether may be removed by blowing dry air on to the electrode.

On no account may the mercury-coated electrode be heated. If the electrode is washed once in 90 p.c. alcohol, and then placed in a beaker of anhydrous acetone for a minute, it may then be dried without using ether. It is always advisable, before weighing, to place the electrode in a desiccator for 20 minutes. The desiccator should have a dish in it containing a little metallic mercury, because even at ordinary temperatures mercury volatilises to a small but appreciable extent.

The mercury can be removed from the electrode by heating in the Bunsen flame, but owing to the tendency for electrolytically deposited mercury to alloy with platinum, the electrode is almost invariably marked with black stains, and a slight loss in weight takes place. For this reason some workers prefer to plate the electrode with copper or silver before using. These difficulties are, however, entirely eliminated by using a mercury cathode; in fact, it is strongly recommended to employ always a mercury cathode when dealing with mercury.

Many electrolytes have been suggested, and all give more or less satisfactory results. Thus, the mercury salt may be dissolved in water and electrolysed in presence of a small quantity of sulphuric, hydrochloric, or nitric acid. With sulphuric acid, from 1 to 2 c.c. of the concentrated acid are added to each 100 c.c. of solution, and electrolysis conducted with a C.D. of 0·3–0·8 ampere per square decimeter, which is finally increased to 1 ampere towards the end of the operation. With rotating electrodes, currents of from 4 to 6 amperes per square decimeter may be employed. The temperature of the electrolyte may be 50°–60°, but not higher. Sometimes, owing to the reducing action of the hydrogen given off at the cathode, mercurous salts are precipitated. The addition of small quantities of ammonium persulphate will cause them to go into solution again. The conditions with the other acids mentioned are very similar to those required for sulphuric acid. Potassium cyanide is not to be recommended, owing to slight solution of the anode taking place.

Sodium sulphide gives very satisfactory results, but care must be taken to employ a very pure solution of salt. From 25 to 30 c.c. of the concentrated solution of sodium sulphide are required for every 100 c.c. of solution. The solution should be heated to about 65°, and for stationary electrodes a C.D. of 0·15–0·25 ampere per square decimeter used. With rotating electrodes from 3 to 6 amperes per square decimeter may be used.

With mercury electrodes rotating anodes are almost invariably used, and high-current densities can be safely employed. The whole of the mercury can be deposited in from 15 to 25 minutes.

Cinnabar may be dissolved in aqua regia, the solution evaporated to dryness. The residue is then taken up with water, filtered from gangue, and then directly electrolysed after the addition of a small quantity of nitric acid.

Gold.

Gold may be deposited from its solution in cyanide or in sodium or potassium sulphide, or in ammonium thiocyanate. The drawback to using potassium cyanide is the tendency for the anode to go into solution. But with low-current densities, this only takes place to a small extent. The solution is made up by adding rather more than the quantity necessary of potassium cyanide to bring the gold salt into a clear solution. With stationary electrodes a C.D. of 0·6–0·8 ampere is employed at a temperature of 50°–60°, the metal being deposited in the course of 2 to 3 hours. With rotating electrodes a current of about 3 amperes may be employed, when the metal will be deposited in about 30 minutes.

Sodium sulphide.—From 20 to 25 c.c. of a saturated solution of sodium sulphide are used for every 100 c.c. of solution. With a C.D. of from 0·1 to 0·3 ampere the metal will be deposited in from 4·5 to 5·5 hours. With rotating electrodes and high-current densities, the results are too high, owing to deposition of sulphur along with the gold.

Ammonium thiocyanate.—5 to 7 grams of ammonium thiocyanate are dissolved in about 80–90 c.c. of water at 70° to 80°, and the gold solution run slowly in with constant stirring. The clear solution is electrolysed at a temperature of 40°–50° with a C.D. of 0·2–0·55 ampere, the metal being deposited in from 1·5 to 2 hours. This method has not been tried with rotating electrodes. The precipitation of small quantities of yellow canarine in the electrolyte during electrolysis does not interfere with the reaction.

E. F. Smith obtains good results by electrolysing a gold chloride solution, using a mercury cathode. In order to prevent the chlorine evolved attacking the anode, from 10 to 12 c.c. of toluene are added. The time required to deposit 0·15–0·2 gram of gold is about 5 to 7 minutes.

Most solvents for gold will also attack the platinum cathode. *Aqua regia,* for example, cannot be used to dissolve the gold from the platinum. F. M. Perkin recommends a dilute solution of potassium cyanide to which is added 4–5 c.c. of hydrogen peroxide, or from 2 to 3 grams of an alkali persulphate. On gentle warming the deposit is removed in a few seconds.

$$2Au + 4KCN + H_2O_2 = 2KAu(CN)_2 + 2KOH.$$
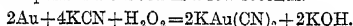
Platinum.

Like gold, platinum can be deposited from solutions containing free mineral acids, but unlike gold, which from these solutions is deposited in a non-adherent form, it may be deposited with very feeble currents in a hard and reguline condition. With high currents and with stationary electrodes the metal is always deposited as platinum black. With a current of from 0·01 to 0·05 at a temperature of 50°–60°, about 0·1 gram of platinum can be deposited in 4·5 to 6 hours. Julia Langness (J. Amer. Chem. Soc. 1907, 459), by using a rotating cathode, deposited 0·2 gram of platinum from a solution of K_2PtCl_6 in 5 minutes. But the current, 17 amperes, must be looked upon as excessive for analytical purposes.

Before depositing platinum it is advisable to coat the cathode with silver.

Rhodium.

This metal may be deposited on to a silver-coated electrode from solutions acidified with phosphoric acid. A current of 0·18 ampere is used. As the process continues, the purple colour of the solution gradually disappears and becomes colourless, when the deposition is finished. With a rotating anode the metal may be deposited from solutions weakly acidulated with sulphuric acid in about 15 minutes with a current of 8 amperes, and with a current of 14 amperes in 5 minutes. The deposited metal has a black colour, but is quite adherent.

Palladium.

In order to obtain a dense and firmly adhering deposit of this metal from acid solutions, it is, according to Amberg (Zeit. f. Elektrochem. 1904, 386, 853, and Annalen, 1905, 235), necessary that the potential should not exceed 1·25 volts. With stationary electrodes the process is very slow, and polarisation at the anode takes place, owing to the formation of oxy- compounds. On the other hand, by using a rotating electrode and solutions of palladium ammonium chloride with 30 p.c. by weight of sulphuric acid and a C.D. of from 0·23 to 0·50 ampere, as much as 0·3–0·9 gram may be deposited in from 3·5 to 5 hours.

Julia Langness, by using currents of from 15 to 17 amperes, and an ammoniacal solution, has obtained quantitative deposits in from 3 to 5 minutes.

Antimony.

This metal may be deposited from its thiosalts, particularly sodium thioantimonite, a method originally suggested by Classen. During the electrolysis there is, however, a danger, owing to the deposition of sulphur at the anode, for sodium thioantimoniate to be formed, and this prevents the quantitative deposition of the metal. A. Fischer (Ber. 1903, 2474) recommends the addition of potassium cyanide to the electrolyte, which prevents the formation of the thioantimoniate, thus:

$$N_2S_4 + 3KCN = 3KCNS + Na_2S.$$
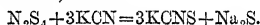
There is one difficulty when sodium sulphide is used—the results obtained are usually slightly too high. This is due to the occlusion of small quantities of sulphur along with the metal. For this reason large quantities of metal should not be deposited by this method. The antimony salt is dissolved in 60–80 c.c. water made just alkaline with sodium hydroxide, any precipitate being ignored, then 20–25 c.c. of a fresh saturated solution of sodium sulphide added, and 2·5–3 grams of potassium cyanide. The solution is then electrolysed at from 30°–40°. With stationary electrodes the metal is deposited in from 4·5 to 6 hours; when rotating electrodes are used, in 30 to 45 minutes.

F. M. Perkin and H. D. Law (Trans. Faraday Soc. i. 262) recommend neutral tartrate solutions. The antimony salt is dissolved in water, and from 8 to 10 grams of ammonium tartrate added; if necessary, the solution is neutralised with dilute ammonia. At a temperature of from 70° to 80°, and a C.D. of 0·25–0·55 the metal can be deposited with stationary electrodes in from 2·5 to 3 hours.

Sand (Chem. Soc. Trans. 1908, 1572) dissolves the metal in 20 c.c. of hot conc. sulphuric acid, and dilutes the cold solution to 80 c.c. The solution becomes turbid owing to hydrolysis, but this disappears during the electrolysis, and does not affect the result. The auxiliary electrode potential is kept at from 0·55 to 0·65, but may be increased to 0·75 toward the end of the process. The time required to deposit 0·35–0·45 gram of metal is from 20 to 35 minutes with an anodic rotation of about 800 revolutions per minute. Small quantities of hydrazine sulphate (0·5–0·6 gram) are added to reduce any antimonial salts which may be formed.

Bismuth.

Until the advent of rotating electrodes, and particularly of the method of graded potential, bismuth was one of the most difficult metals to deposit, since it almost invariably came

down in a powdery and non-adherent form. These remarks do not apply to the mercury cathode. According to Kollock and Smith (J. Amer. Chem. Soc. 27, 1539) to a solution containing about 0·2 gram of the metal as nitrate, the volume of which should not exceed 12 c.c., 0·5 c.c. of strong nitric acid is added. A current of about 4 amperes is passed, and the whole of the bismuth will be precipitated in from 12 to 15 minutes. The anode should be very rapidly rotated, so that the mercury may take up the bismuth as it separates, otherwise it may collect in a black mass beneath the anode.

Sand (Chem. Soc. Trans. 1907, 373) uses a solution containing tartaric acid; any excess of nitric acid, which may be in the original solution, is removed by the addition of sodium tartrate. By means of the auxiliary electrode, the cathode potential is maintained between 0·63 and 0·9 volt. The anode is rotated at 800 revolutions per minute. In one case the amount of metal in the solution was 0·2 gram, 2·5 c.c. of nitric acid (1 : 4) was added, and 8 grams of sodium tartrate. With a current varying from 0·2 to 3 amperes the metal was deposited in 9 minutes.

A. Fischer uses an electrolyte containing for each 0·5 gram metal, 10 grams of potassium oxalate, and 5 grams of Rochelle salt. By means of an auxiliary electrode, the cathode potential is kept at 0·8 volt. Temperature of solution, 75°; time required, 11 to 15 minutes.

Tin.

Tin can be satisfactorily deposited from an ammonium sulphide solution. Sodium sulphide is not satisfactory; indeed, tin is not thrown out from strong solutions at all. Hence, we have here a method of separation of antimony and tin. If the tin solution is acid, it is first neutralised with ammonia, and then sufficient yellow ammonium sulphide is added to dissolve the precipitate and form a clear solution. With stationary electrodes and a current of 1·0–1·8 amperes, the tin will be deposited in from 3 to 4 hours.

With rotating electrodes the metal can be deposited in from 15 to 35 minutes, depending upon the current employed, and the temperature of the electrolyte. Currents of from 1·8 to 8 amperes have been successfully employed.

A mercury cathode also gives very good results. The tin salt is dissolved in dilute sulphuric acid, and electrolysed with a current of from 2 to 5 amperes. From 0·5 to 0·8 gram can be deposited in from 8 to 12 minutes.

When platinum electrodes are employed, considerable difficulty may be experienced in removing the deposit. The simplest method is to make the electrode on which is the deposit, the cathode in dilute sulphuric acid, a piece of copper wire serving as cathode. Some workers prefer to coat the electrode with copper, and then the copper with tin, the tin being deposited from an ammonium oxalate solution; this proceeding, however, is tedious.

Tellurium.

Finely powdered tellurium is dissolved in a few c.c. of conc. sulphuric acid. The white anhydride so obtained is washed with a little freshly boiled water into the electrolysing vessel, and then 80 c.c. of a 10 p.c. solution of pyrophosphoric acid or sodium pyrophosphate added. The solution is then electrolysed with a C.D. of 0·1 ampere. Time of deposition, 4 to 5 hours. When a rotating electrode is employed, the time of deposition is much accelerated.

GROUP II.—**Zinc.**

Zinc is rather a difficult metal to deposit satisfactorily and quantitatively, and a very large number of methods have been suggested by different workers. Although it is +0·77 volt more positive than hydrogen, it can be deposited from slightly acid solutions, owing to the high supertension of hydrogen evolution from the surface of zinc, the supertension of hydrogen being 0·70 volt.

With zinc it is advisable always to employ rotating electrodes. The electrodes need not, however, be made of platinum; nickel, particularly in the form of gauze, answers equally well.

Price and Judge (Trans. Faraday Soc. 1907,) use an electrolyte containing sulphuric acid which must not be more than $\frac{1}{3}N$ and sodium sulphate.

It is, in fact, better to keep the normality of the acid rather lower than one-sixth. By starting with a C.D. of 0·25 ampere and increasing to 2·0 amperes about 0·2 gram of metal can be deposited in 40 minutes.

Owing to acetic acid being much less dissociated than sulphuric acid, solutions containing considerable quantities of this acid may be used. Thus, Exner (J. Amer. Chem. Soc. 1903, 896) deposited 0·25 gram zinc with a current of 4 amperes in 15 minutes. The electrolyte contained 3 grams sodium acetate and 0·30 p.c. acetic acid. A. Fischer (Chem. Zeit. 1907, 25) takes 1 c.c. conc. sulphuric acid, 3·5 c.c. conc. ammonia, 1·5 c.c. acetic acid, and 2·5 grams ammonium acetate. A. Classen (Quant. Analyse d. Elektrochem. 1897, 156) uses a solution of potassium oxalate, the zinc solution is added to a solution of from 4 to 5 grams of potassium oxalate. As soon as the electrolysis has started, it is advisable to add a few c.c. of a 1 p.c. solution of oxalic acid. Ammonium salts must be absent.

Kollock and Smith use a mercury cathode, and a solution of zinc sulphate or zinc sulphate acidified with sulphuric acid.

Zinc adheres somewhat firmly to platinum electrodes, and, if left on for some time, seems to alloy with the electrodes. If, however, it is removed shortly after the electrolysis, no ill effect is produced. The best method to remove the deposit is to warm the electrode in a strong solution of sodium hydroxide.

Cadmium.

Although cadmium is electropositive to hydrogen by as much as 0·42 volt, yet, owing to the high supertension of hydrogen with this metal, it is possible to deposit it from acid solutions. Owing, however, to the depolarising action of nitric acid, nitrates should not be present; on the other hand, small amounts of chlorides do not seem to matter.

Cadmium may be deposited from solutions containing small quantities of free sulphuric acid. It is usually advisable to add, after the bulk of the cadmium has been deposited, the equivalent amount of sodium hydroxide to neutralise the sulphuric acid which has been set free through the deposition of the metal. In 100 c.c. of solution, 1 c.c. of concentrated

sulphuric acid may be added before commencing the electrolysis. With stationary electrodes and a current of 0·1 to 0·35 ampere, the metal is deposited in from 3 to 4 hours; with a rotating electrode and a current of 4 to 5 amperes, the deposition is complete in 20 minutes. The deposition from cyanide solutions is the simplest and most easy to carry out. A solution of potassium cyanide is added to the cadmium solution until the precipitate first produced is dissolved, and then about half the quantity already added is run in. It is advisable also to add about 2 c.c. of a normal solution of sodium hydroxide. With stationary electrodes and a current of 0·15–0·35 ampere at a temperature of 50°, the deposit is complete in from 4·5 to 5·5 hours; with rotating electrode and a current of from 5 to 8 amperes, in from 15 to 30 minutes.

GROUP III.—Iron.

It is not often that the analyst requires to deposit iron electrolytically, owing to the very satisfactory methods of titration and precipitation. Iron cannot be deposited from acid or even from neutral salt solution upon a platinum electrode, owing to its being so much more electropositive than hydrogen—0·34 volt, while the supertension of hydrogen is only 0·08 volt. Kollock and Smith (Proc. Amer. Phil. Soc. 44, 149, and 45, 261) have, however, succeeded in depositing iron from weak acid solutions by means of a mercury cathode, the iron as it is deposited amalgamating with the mercury. The method described by these authors is as follows :—

Five c.c. contained 0·2075 gram of iron. Three drops (40 drops=1 c.c.) of concentrated sulphuric acid were added to it, when it was electrolysed with a current of 3 to 4 amperes and 7 volts. The anode made from 500 to 900 revolutions per minute. The iron was completely deposited in 7 minutes. The water was then siphoned off and the amalgam washed, as in all previous cases, with alcohol and water.

From its oxalate, tartrate, or citrate solutions, iron may be satisfactorily deposited, but in all cases traces of carbon are deposited along with the metal. By employing low-current densities, the amount of carbon deposited from oxalate and tartrate solutions is negligible, but from citrates the results are almost always considerably too high.

Ammonium oxalate.—This method was first suggested by Classen (Zeit. f. Elektrochem. i. 288), and is the one most generally employed. The iron solution, which should be free from chlorides and nitrates, must be poured into the solution of ammonium oxalate, if it is in a ferrous condition, otherwise a precipitate of ferrous oxalate may be formed which is difficult to dissolve. With ferric salts the order of adding does not matter.

Dissolve 5–7 grams of ammonium oxalate or acid ammonium oxalate in a small quantity of hot water, and to this add the iron salt also dissolved in a little water. The solution is then made up to the required bulk, and electrolysed with a C.D. of from 0·6 to 1·2 amperes. Time of deposit from cold solutions and with stationary electrodes, 4 to 5 hours; from solutions at 50°–60°, in 2 to 2·5 hours. As the electrolysis proceeds, it will sometimes be

noticed that a small quantity of ferric hydroxide separates. This is due to the solution becoming slightly alkaline, owing to the decomposition of the oxalate by the current. Should the hydroxide be thrown out, small quantities of oxalic acid must be added.

With rotating electrodes the time of electrolysis is from 14 to 20 minutes.

With tartrate solutions the results are equally good. The method of procedure is similar to that described for oxalates, ammonium tartrate being used in place of the oxalate. The advantage of the tartrate method is that ferric hydroxide is never deposited; consequently, it is not necessary to add tartaric acid, and thus less attention is required.

Nickel.

Nickel and cobalt are difficult to determine by general analytical methods, but they can both be readily and accurately analysed by electrochemical means.

Although many methods have been suggested for the deposition of nickel, few of these are of practical importance. Most of them depend upon the use of the salts of organic acids. In such cases there is a tendency for traces of carbon to be deposited with the metal. The most useful and generally applicable method for depositing nickel is that of Fresenius and Bergmann (Zeit. f. Anal. Chem. 33, 9), in which the double salts of potassium and nickel or ammonium sulphate together with excess of ammonia are used.

The nickel salt is dissolved in water and mixed with an aqueous solution of from 4 to 5 grams of ammonium sulphate, and from 30 to 35 c.c. of strong ammonia. If more than 1 gram of the nickel salt is employed, larger quantities of ammonia should be added. As, however, large quantities of strong ammonia are apt to contaminate the atmosphere, it is better to work with smaller quantities of nickel. Nitrates should be absent, as their presence considerably retards the rate of deposition. With a current of 1–1·5 ampere per sq. dcm., the metal will be deposited in from 2 to 2·5 hours; at a temperature of 50°–60°, the time will be from 1·5 to 2 hours; with rotating electrodes, in from 15 to 30 minutes, depending upon the conditions and the form of apparatus. The metal is usually deposited as a brilliant plating on the electrode. The deposit is at times somewhat difficult to remove, and, owing to its appearance being rather like polished platinum, it is not always easy to ascertain whether it has been completely dissolved off. The best method of removing the metal is to warm the electrode in moderately strong sulphuric or nitric acid.

Other methods employed are the double oxalate method of Classen and Von Reiss (Ber. 14, 1622); ammonia and ammonium borate, by F. M. Perkin and W. C. Prebble (Trans. Faraday Soc. 1904, 103). Kollock and Smith (Proc. Amer. Phil. Soc. 45, 262) have used a mercury cathode successfully, the time of deposition being from 7 to 20 minutes. An amalgam of 40 grams mercury and 1 gram nickel has the consistency of soft dough, and is bright in appearance.

Cobalt.

Cobalt may be deposited from an ammonium sulphate, ammonium hydroxide solution similar

to that used in the case of nickel. But as a rule the results obtained are too low, owing to the tendency for peroxide to be formed on the anode.

F. M. Perkin and W. C. Prebble (Trans. Faraday Soc. 1905, 103) use a solution con-

adding 2 c.c. of a 5 p. _____ _____ acid to the solution of the cobalt salt in 70–80 c.c. water and then 20–25 c.c. of a 10 p.c. solution of dihydrogen sodium phosphate. The electrolysis should be commenced cold with a current density of 0·2–0·3 ampere per sq. dcm.; after about 50 minutes the solution is warmed to 50° or 60°, and the current increased to 1·2 ampere. If, as often happens, some peroxide is deposited on the anode, it can be removed by the addition of 0·2–0·3 gram of hydroxylamine sulphate. After the solution has become colourless, about 1 c.c. of $N/1$-ammonia should be added. The time necessary with stationary electrodes is from 4 to 5 hours. The deposit is extremely bright, resembling polished platinum.

The only methods which have been tried with rotating electrodes are solutions containing ammonium acetate and solutions with sodium formate. With currents of 8 amperes, L. Kollock and E. F. Smith (J. Amer. Chem. Soc. ·29, 797) succeeded in depositing 0·3 gram of cobalt in from 30 to 40 minutes.

GROUP IV.—Lead.

Owing to its ready oxidisability, it is difficult to deposit lead satisfactorily on the cathode. Except in cases of separation from other metals, indeed, it is of no advantage to deposit it at the cathode. Sand has, however, found it a convenient method to separate lead from cadmium and bismuth (Chem. Soc. Proc. 22, 43).

From dilute solutions of nitric acid lead is partially deposited as metal on the cathode, and partially as peroxide at the anode. It is therefore necessary to have about 20 c.c. of nitric acid (1 : 4) to every 100 c.c. of electrolyte. Arsenic, manganese, selenium, and bismuth should be absent, and according to Vortmann (Annalen, 351, 283), antimony, silver, mercury, zinc, iron, cobalt, aluminium, and the alkali metals also cause the results to be high. Chromic acid should also be absent, and phosphoric acid retards the deposition. The lead salt is dissolved in water, and from 25 to 30 c.c. of strong nitric acid added. The electrodes used, whether stationary or rotating, should be roughened by the sand blast. With stationary electrodes and a current of from 1·3 to 1·8 ampere at a temperature of 60°–70°, the deposition will be complete in from 1 to 1·5 hours. At the commencement of the electrolysis a yellowish deposit is obtained which becomes orange or red, and finally dark-brown or black.

With rotating electrodes, the time of deposition is from 10 to 25 minutes.

At the end of the electrolysis the electrode is well washed by placing it in hot water, then washed with alcohol and ether, and heated to 220° in the air-bath for an hour. It must be cooled in a desiccator; the weight of the deposit is multiplied by the factor 0·866.

The best method to remove the deposit from the electrode is to warm it with equal volumes of nitric acid and water to which 4–5 grams of glucose has been added.

Lead does not give satisfactory results with a mercury cathode.

Manganese.

Manganese can only be deposited as oxide the anode. It is, however, much more difficult to deal with than lead, as the deposit is apt not to adhere well. It is absolutely essential to employ roughened electrodes. Mineral acids cannot be employed. The most satisfactory electrolyte is one containing ammonium acetate, and Engels (Zeit. Elektrochem. ii. 413) has shown that the addition of small quantities of chrome alum helps to cause the deposit to adhere more firmly, probably owing to a depolarising effect. The manganese salt is dissolved in 40–50 c.c. of water, 8–10 grams of ammonium acetate added, and the solution electrolysed at a temperature of 75°–80°, with a current of 0·6 to 1 ampere. The deposition will be complete in from 1·5 to 2 hours.

With rotating electrodes the time will be about 30 minutes. In this case it is as well to add 10 c.c. alcohol to prevent frothing (J. Koster, Zeit. f. Elektrochem. 10, 553).

The best way to ascertain if all the manganese has been deposited, is to employ the permanganate test. Withdraw 1 or 2 c.c. of the solution, add 3 c.c. conc. nitric acid, and about 1 gram of red lead. Boil for a minute or two and dilute. A pink colouration indicates that the whole of the manganese has not been removed.

When all the manganese has been deposited, the electrode is washed as usual, and then strongly heated in order to convert the hydrated manganese peroxide into trimanganese tetroxide Mn_3O_4. It is necessary to heat until the black deposit becomes a dull orange red. The weight of the deposit multiplied by 0·72 gives the weight of metallic manganese.

Chromium.

This metal cannot be deposited on the anode as peroxide; neither under ordinary conditions is it possible to obtain a cathode deposit. Kollock and Smith (Trans. Amer. Chem. Soc. 27, 1905, 1255) have succeeded in depositing it in the form of an amalgam by employing a mercury cathode. The electrolyte consisted of dilute sulphuric acid. With a current of 1–3 amperes 0·12 gram was deposited in 20 minutes. This method is useful for separating chromium from aluminium, which latter metal is not deposited as an amalgam.

Classen (Ber. xxvii. 2060) oxidises chromic salts to chromates in an ammonium oxalate solution. This method is useful for separating chromium from iron, nickel and cobalt, and in the analysis of chromium steels and of chrome iron ore. The chromic acid produced can be estimated iodometrically or by precipitation as lead or barium chromate.

The solution containing the iron and chromium salt has excess of ammonium oxalate added to it, and if free mineral acid is present is neutralised with ammonia. It is then electrolysed, when the iron is deposited at the cathode and the chromium oxidised to chromate. The iron, when deposited in presence of chromium salts, is usually very brilliant like polished platinum. When all the iron is deposited, the

solution is removed, the iron deposit dried and weighed, and the chromium determined. If the whole of the chromic salt has not been oxidised during the deposition of the iron, the solution is again electrolysed. By using a rotating anode it is possible to completely oxidise 0·15 gram of a chromic salt, such as $Cr_2(SO_4)_3$ or Cr_2Cl_6 in 90 minutes, the volume of the solution being 120 c.c. and the amount of ammonium oxalate 15 grams. The electrolyte should be heated to 80°, and a current of from 5 to 5·5 amperes employed (Elektronalytische Schnellmethoden, p. 180).

Uranium.

Uranium is deposited at the cathode as oxide from solutions containing acetic acid or ammonium carbonate. The deposit consists of $U_3O_4,3H_2O$. At the end of the operation this is heated strongly to convert it into U_3O_8.

Wherry and Smith (Trans. Amer. Chem. Soc. 29, 806), by using a rotating cathode and an electrolyte containing in 125 c.c. 2·5–5·5 gram sodium acetate, deposited 0·25 gram of uranium in from 15 to 30 minutes, the current employed being 3–5 amperes, the electrolyte being either cold or heated to 50°.

Molybdenum.

From solutions containing dilute sulphuric acid, molybdenum can be deposited as peroxide at the cathode, but the deposit cannot be weighed as such. Wherry and Smith (Trans. Amer. Chem. Soc. 29, 806), therefore, oxidise it by means of nitric acid and weigh as MoO_3.

Thallium.

Many methods have been suggested for the electrolytic analysis of thallium, but only one can be considered satisfactory, and that is, by using a mercury cathode. By depositing the metal into pure mercury, it is found that portions are lost on weighing ; but if the mercury contains a small quantity of zinc, this is not the case. Smith recommends to deposit the zinc and mercury simultaneously. In order to do this a definite volume of zinc sulphate solution of known strength is added to the solution before electrolysis. The electrolyte consists of dilute sulphuric acid. The amount of zinc necessary to protect the thallium is very small, and need not be more than 0·001 gram. With a current of 5 amperes it is possible to deposit as much as 0·2 gram in about 10 minutes. It is, however, advisable to electrolyse for a longer time.

GROUP V.—**Sodium.**

E. F. Smith (Trans. Amer. Chem. Soc. 25, 1903, 890) was the first to show that the metals of the alkali group could be analysed electrolytically. The method is based on the removal of the halogen anion of the metal by causing it to unite with silver, the alkali metal remaining in the solution as hydroxide is determined by titration ; by ascertaining the increase in weight of the silver anode, the halogen can be also determined.

An ingenious apparatus has been devised by Hildebrand (Trans. Amer. Chem. Soc. 29, 1907, 447) for the analysis of the cations of the alkali metals, and of barium and strontium ; and at the same time of various anions. In principle the cell resembles that of the Castner-Kellner process employed in the manufacture of sodium hydroxide.

The outer cell (Fig. 68) consists of a crystal-

lising dish, 11 cm. in diameter and about 5 cm. high, with the bottom cut off, is placed inside, and rests on a triangle of glass rod placed on the bottom of the crystallising dish. The beaker is kept in position in the middle of the dish by means of three rubber stoppers fitted radially between it and the outer dish. Two compartments are thus formed, which are sealed off by means of mercury. In the outer compartment there is a ring consisting of six turns of stout nickel wire, provided with three legs dipping into the mercury and serving to maintain the lowest winding of

FIG. 68.

the nickel about 1 cm. above the surface of the mercury, when sufficient is placed in the dish to seal off the two compartments. By means of a platinum wire passing through a glass tube the mercury is made the cathode. The anode consists of two discs of platinum gauze heavily plated with silver.

Pure mercury must be used, and the cell must be kept scrupulously clean. Before starting the cell, mercury is poured in so that its level is about 3 mm. above the lower edge of the inside beaker. The solution to be electrolysed is then put into the inner compartment. In the outer one enough distilled water to cover the nickel wire is placed, and to this 1 c.c. of a saturated solution of common salt. By this arrangement the amalgam formed in the inner compartment is immediately decomposed in the outer one. The sodium chloride serves merely to make the liquid a conductor, so that the action may proceed more rapidly at the commencement. Unless this is done, the amalgam is not entirely decomposed in the outer compartment, because pure water does not attack it rapidly enough to prevent the partial decomposition in the inside cell. After the electrolysis is complete, the entire contents of the cell are poured into a beaker, the cell rinsed, and the alkali titrated. After titration the mercury is washed, the water decanted, and the metal poured into a large separating funnel from which it can be drawn off clean and dry.

The table on p. 257 give the results which were obtained by Hildebrand.

The weighed gauze anode is clamped to the shaft. The latter is lowered into the cell till
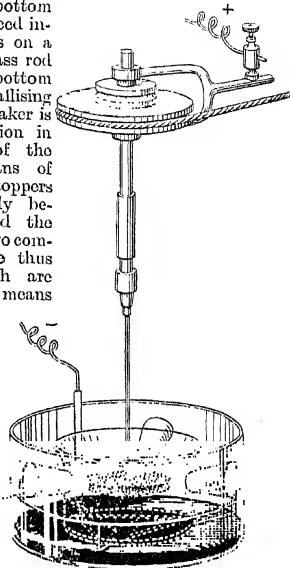
the lower gauze is about 5 mm. from the surface of the mercury. The most convenient speed for the motor is about 300 revolutions per minute. The anode does not require washing, as the water after electrolysis is pure. It may be at once dried in the steam oven.

Time : Mins.	Volts	Amperes	Sodium in grams		Chlorine in grams	
			Present	Found	Present	Found
30	4·0–2·5	0·50–0·02	0·0461	0·0459	0·0708	0·0704
45	3·5–2·5	0·34–0·01	0·0461	—	0·0708	0·0706
40	3·5–3·0	0·50–0·01	0·0461	—	0·0708	0·0704
45	4·0–3·5	0·65–0·01	0·0461	—	0·0708	0·0716
30	4·0–2·5	0·76–0·02	0·0461	—	0·0708	0·0713
55	3·0	0·26–0·02	0·0461	—	0·0708	0·0709

By means of this apparatus the halogen salts of the alkali metals can be analysed. Also the halogen salts of barium and strontium. In fact, any anion with any metal which will unite with silver to form an insoluble salt can be analysed, provided, of course, that the metallic salt is soluble, and that the metal will form an amalgam with the mercury. In the case of the alkali metals and of strontium and barium, the hydroxides of which are soluble in water, the cations are analysed by titration. With other metals forming amalgams which are not readily decomposed this method of analysis is not to be recommended, because, in the first place, the considerable quantity of mercury necessary is inconvenient to weigh, and, secondly, it requires to be kept very pure, consequently the continual purification of such large quantities of mercury would be tiresome.

Analysis of anions when united with heavy metals. The SO_4 anion in such salts as copper sulphate may be analysed by electrolysing a known weight of copper sulphate dissolved in water with a mercury cathode and a platinum anode as already described. When all the copper has been deposited, the solution is siphoned off, the amalgam washed with water, and the wash water added to the original solution. The whole of the anode solution is then titrated with N-sodium hydroxide. The copper can, of course, be estimated by weighing the amalgam.

Separation of sodium from calcium and magnesium. When calcium and magnesium salts are electrolysed in Hildebrand's apparatus, it is found that the hydroxides of these metals are precipitated in the inner cell. It has therefore been found possible to separate sodium from these metals by means of this apparatus. The outer cell contains all the sodium as hydroxide, and the sodium can be determined by titration. The analytical results obtained are practically theoretical.

In a similar manner barium can be separated from calcium and magnesium.

Arsenic.

It is not possible to deposit arsenic quantitatively in the metalloid condition, neither can it be precipitated at the anode as oxide. Arsenic is readily converted by nascent hydrogen into arseniuretted hydrogen, its gaseous hydride, AsH_3; hence, electrolytic methods of analysis are not usually employed for analysing arsenic compounds. It is, however, possible to estimate

Vol. I.—*T.*

very small quantities of arsenic contained in food, &c., by electrolysis. The process consists in evolving electrolytic hydrogen in presence of the arsenic, whereby the arsenic is converted into arseniuretted hydrogen. The gaseous hydride is then passed through a glass tube, heated by a small Bunsen burner, as in the Marsh apparatus, whereby the arsenic is deposited upon the tube in the form of a mirror. In order to estimate the amount of the arsenic, the mirror is then compared with mirrors prepared from known quantities of arsenic.

In 1812 Fischer (Gilbert's Ann. 42, 92) suggested the employment of the electric current to detect the presence of very small quantities of arsenic. It was again suggested by Bloxam (Quart. Journ. Chem. Soc. 1861, 13, 12 and 338) in 1861, but the apparatus had several disadvantages, and never came into practical use. Since then various modifications have been suggested by different authors, and, in 1903, Thorpe (Journ. Chem. Soc. 1903) describes a new form of apparatus which has been successfully employed for the analysis of traces of arsenic in food, beer, and other substances.
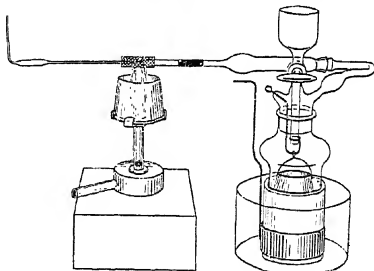
Fig. 69.

It consists of a platinum cathode hung in a glass cylindrical vessel, which is open at the end, and lets into a Pukal porous cell. The porous cell is surrounded by the anode, and stands in an outer vessel. The upper portion of the cylinder is open, and has a ground neck for the insertion of the drying tube filled with anhydrous calcium chloride, and also carries the funnel, which is fitted with a tap, through which the solution to be tested is run in. A capillary tube is connected to the end of the calcium chloride tube. The middle of this tube is heated by means of the small Bunsen burner, and is surrounded where the flame heats it with a piece of platinum or iron-wire gauze, to prevent the tube being fused. The whole apparatus is placed in a vessel containing cold water, to prevent undue heating during electrolysis.

Method of working. The apparatus is carefully washed with distilled water. The outer cell E is filled with dilute sulphuric acid (30 p.c.), then the inner cell. (The porous cell should be soaked in dilute sulphuric acid for about half an hour before being used.) As soon as all the connections are made, the Bunsen burner is placed in position, but not lighted, and the current is passed. A current of about 5 amperes should be used; the escaping hydrogen thereby

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produces a flame of about 3 mm. in size. As soon as all the air has been driven out, which usually occupies about 10 minutes, the issuing hydrogen is ignited and the Bunsen burner lighted. If after about 15 minutes no brown ring makes its appearance, the reagents may be considered free from arsenic. At the end of 30 minutes the capillary tube is sealed off, and the open end also fused together. The mirror is then compared with the standard mirrors as above described.

Preparation of standard mirrors. Pure resublimed arsenious oxide is ground in an agate mortar and dried at 100°. Then 0·1 gram is carefully weighed and washed into a 1-litre flask, the flask being filled to the mark with distilled water. Each 1 c.c. of this solution contains 0·0001 arsenious oxide ; 100 c.c. of this solution are diluted to 1 litre. This second solution contains 0·00001 gram of arsenious acid in each 1 c.c., or 0·01 mg. Standard tubes containing 0·004, 0·006, 0·008, 0·010, &c., mg. can then be prepared.

When foodstuffs are being examined for arsenic, Thorpe considers it advisable to take a portion of the foodstuff—arsenic free—and mix it with the known quantity of arsenic before proceeding to electrolyse it. The standard mirrors are thus prepared under the same conditions as those under which the suspected foodstuff is tested.

S. R. Trotman (J. Soc. Chem. Ind. 23, 177) recommends the adoption of a parchment membrane in place of the porous Pukal cell, as he considers this decreases the resistance, and thus makes the apparatus more sensitive. It is, however, not so convenient to use.

Sand and J. E. Hackford (Chem. Soc. Trans. 85, 1018) use the parchment membrane, but they also employ a heavy lead cathode and a lead anode. Their apparatus is thereby much cheaper than that used by Thorpe, and is said to be equally accurate.

Metallic Separations.

A large number of separations of metals by electrolytic methods have been worked out, but in many cases a purely chemical procedure or a combination of electrolytic and chemical methods is easier. There are, however, cases in which satisfactory and rapid electrolytic separations can be carried out. A few of the more important are given below.

Copper from nickel. By employing a rotating anode with an auxiliary electrode, and maintaining the cathode potential at 0·7–0·75 volt, copper can be deposited from solutions containing sulphuric acid. The solution is then made alkaline with ammonia, when the nickel can be deposited. If the cathode potential is not regulated, small quantities of the nickel are deposited along with the copper.

Exner (J. Amer. Chem. Soc. 25, 896) finds that by employing a solution containing nitric acid and ammonium nitrate (volume of solution 125 c.c.; HNO_3, 0.25 c.c. ; 3 gram NH_4NO_3) and using a rotating anode, it is possible to deposit as much as 0·25 gram copper in 15–20 minutes ; the nickel, which may be of equal weight, remains in solution, and can be afterwards deposited.

Copper from lead. Since lead is deposited from solutions containing nitric acid as peroxide on the anode, whilst copper is deposited as metal at the cathode, it might be supposed that there would be no difficulty in depositing both metals concurrently. It must, however, be remembered that unless there is a considerable concentration of nitric acid, a portion of the lead will be deposited as metal at the anode. On the other hand, in presence of copper, the tendency to reduction of the lead and its appearance at the cathode is decreased ; that is to say, in presence of copper a lower concentration of nitric acid is required. It has, therefore, been found possible to separate the two metals. The volume of solution employed was 85 c.c., and contained 1 c.c. HNO_3 (1 : 4). With a rotating anode and a current of 2 amperes, the whole of the lead was deposited in 5 minutes. The current was then increased to 10 amperes, when the last traces of copper were removed. The washing and drying of the anode deposit requires care, since the peroxide when deposited from weak acid solutions does not adhere so well as from stronger solutions (Sand).

Copper and arsenic. McCay finds the following conditions give a satisfactory deposit of copper in presence of arsenic. The arsenic remaining in the solution cannot, however, be estimated electrolytically, unless present in very small quantities.

To the solution 20 c.c. ammonium hydroxide (sp. gr. 0·91) and 2·5 gram ammonium nitrate are added, the volume of solution being 125 c.c. The solution is then electrolysed at a temperature of 50°–60°, with 0·5 ampere per 100 sq. deem. of electrode surface. As much as 0·22 gram of copper will be deposited in 3 hours. With a rotating anode about 15 minutes are required. In this solution the arsenic should be present as arsenate. Copper and arsenic may also be separated electrolytically from solutions containing potassium cyanide. If acid, the solution is neutralised, and then sufficient potassium cyanide added to just redissolve the precipitate first produced. With a current 0·25–0·27 ampere, the whole of the copper is deposited in about three hours.

Antimony from tin. Tin can be quantitatively deposited from solutions containing excess of ammonium sulphide. It cannot, however, be deposited from solutions containing excess of sodium sulphide. Antimony, on the other hand, can be deposited from solutions containing excess of sodium sulphide. It is therefore possible to separate antimony from tin by adding excess of sodium sulphide to a solution containing the two metals. If the solution is acid, it is first made slightly alkaline with sodium hydroxide before the sodium sulphide is added. It is, however, better to first precipitate the two metals as sulphides, and then dissolve them in a concentrated solution of sodium sulphide. The tin should be in the stannic state. The solution is electrolysed at a temperature of 50°–60° with a current of from 0·2 to 0·9 ampere per sq. dem. of electrode surface. In from 2 to 4 hours the whole of the antimony is deposited. It is, however, almost always contaminated with small quantities of tin.

In order to deposit the tin, the sodium sulphide must be decomposed. This is done by adding about 25 grams of ammonium sulphate,

and boiling until no more hydrogen sulphide is evolved. The tin is now deposited by electrolysing with a current density of from 0·3 to 0·5 amperes.

The best method of separating antimony and tin is that of Sand, by means of graded potential and a rapidly rotating anode (Chem. Soc. Trans. xciii. (2) 1908, 1572). From solutions containing strong sulphuric acid (1 : 1) antimony is deposited at an auxiliary potential of 0·65 volt when the temperature is kept above 100°, and a small quantity of hydrazine sulphate is added. Tin, on the other hand, under similar conditions, is not deposited below 0·8 volt. The method of procedure when dealing with alloys of antimony and tin is as follows :—

The alloy is dissolved in a mixture of 40 c.c. conc. sulphuric acid, 5 c.c. water, and 2 c.c. nitric acid (1 : 42) ; on heating to 180°–200° solution rapidly takes place. It is necessary to remove the nitric acid because it causes the formation of antimonic acid, which is only slowly reduced to the metallic state electrolytically. In order to decompose the nitric acid (nitrosulphonic acid), a current of 5 amperes is passed, and the liquid heated to 250°–270°. After the current has been passed for 5 to 10 minutes at the high temperature, it is stopped. The solution is cooled to 100°, and 0·5 gram of hydrazine sulphate added. (N.B.—The amount of hydrazine sulphate added should be equal to the weight of metal taken.)

The temperature is then raised to 300°. It is again cooled to 100°, when from 30 to 40 c.c. of water and another 0·5 gram of hydrazine sulphate are added.

The anode [1] is then rotated to ensure mixing of the solution, the temperature of which rises to about 120°. The analysis is now begun, the auxiliary potential having first been adjusted to 0·53–0·65 volt. The current will vary between 3–4 amperes, and, at the end of the electrolysis, will drop to 0·4–0·5 volt. Time of electrolysis from 20 to 30 minutes.

The tin is determined as follows: The solution after the antimony has been deposited is mixed with about 4 grams of oxalic acid, and is neutralised with strong ammonia. In order to prevent loss by spurting the electrodes are placed in position, the rotating stem being passed through a hole drilled in a clock glass. The ammonia is poured on the clock glass and runs down the stem of the electrode into the solution, the anode or inner electrode being at the same time rotated. Considerable ebullition ensues, but none of the liquid is spurted out. Exact neutralisation is ascertained by the use of methyl orange as indicator. Litmus cannot be employed, since its colloidal nature hinders the deposition of the tin. After neutralisation, 0·5–0·75 c.c. of sulphuric acid are added for every gram of oxalic acid previously added.

The solution is electrolysed at a temperature of 70° with a current of 3–4 amperes. Time of deposit, 60–80 minutes.

Silver and copper. (Smith and Frankel, Amer. Chem. J. 12, 104.) To a neutral solution of the silver and copper salt, add 2–3 grams of pure potassium cyanide. Electrolyse at a temperature of 65° with a current of 0·03–0·05

ampere, and maintain the potential at 1·1–1·6 volt. The silver will be completely deposited in from 4 to 5 hours. After the silver has been weighed, the electrode is replaced, the current and voltage increased, when the copper will be deposited.

Silver may also be separated from copper in ammoniacal solutions by using an auxiliary electrode, and keeping the potential below 0·5 volt.

Iron from other metals. Iron can readily be separated from aluminium, vanadium, glucinum, uranium, thorium, and many other metals with which it may be alloyed by dissolving in sulphuric acid, filtering from any residue, nearly neutralising with ammonia, and electrolysing with a mercury cathode.

Cadmium from zinc. These metals can be separated by means of graded potential. The solution is made up by adding first 2 c.c. of conc. sulphuric acid, then 3·33 grams of sodium hydroxide, and 1 c.c. of glacial acetic acid. The auxiliary electrode is kept at a potential of 1·15 –1·20 volts, and the solution electrolysed at a temperature of 30°. The whole of the cadmium will be deposited in 11–14 minutes. The potential is afterwards raised, when the zinc can be deposited in about 30 minutes.

Bibliography.—Electroanalysis, by Edgar Smith (P. Blakiston's Son & Co., Philadelphia) ; Practical Methods of Electrochemistry, by F. Mollwo Perkin (Longmans, Green, & Co.,London); Elektroanalytische Schnellmethoden, by A. Fischer (Ferdinand Enke, Stuttgart) ; Quantitative Analyse durch Elektrolyse, by A. Classen (Julius Springer, Berlin) ; Analyse des Métaux par Électrolyse, by A. Holland et L. Bertiaus (H. Dunod et E. Pinat, Paris). F. M. P.

ANAMIRTA COCCULUS or A. PANICULATA (Colebr.). The former is the superseded name, and the latter the true name, of the Indian Menispermaceous liane, whose dried fruits (Grains of Paradise) are supplied under the name of *Cocculus indicus* (v. COCCULUS INDICUS).

ANANAS, OIL or ESSENCE OF. A solution of ethyl butyrate in 8 to 10 times its weight of alcohol. It possesses the odour of the pineapple (*Ananas sativus* (Schult.)), and is employed in confectionery and perfumery ; also to imitate the flavour of rum (Hofmann, Annalen, 81, 87).

ANANDONIS GREEN, *Hydrated chromium sesquioxide (v.* CHROMIUM*).*

ANASPALIN. Trade name for a form of wool-fat.

ANATASE or *Octahedrite.* One of the trimorphous forms of titanium dioxide (TiO_2) met with as crystallised minerals ; the others being rutile and brookite. It is found as small, isolated crystals of a steel-blue or honeyyellow colour, in schistose rocks, particularly in the Alps. L. J. S.

ANCHIETA BARK. The root bark of *Anchietea salutaris* (A. St. Hil.), one of the Violaceæ, a bushy shrub growing at Rio de Janeiro. It contains *anchietine*, a substance crystallising in straw-coloured needles, having a nauseous taste. Used for syphilis and quinsy (Peckolt, Arch. Pharm. [2] 97, 271).

ANCHUSIN (*Alkannin*) *v.* ALKANNET.

ANDA-ASSU, OIL OF. An oil obtained from the seeds of *Joannesia Princeps* (Vell.), belonging to the Euphorbiaceæ, growing in Brazil. It is clear, slightly yellowish, odourless, with a taste

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[1] After the metal has dissolved, the subsequent operations are carried out with the electrodes in position.

at first nauseating and then sweet. It solidifies at 8°, its sp.gr. at 18° is 0·9176 (Pharm. J. [3] 12, 380).

ANDAQUIES WAX v. WAXES.

ANDROGRAPHIS PANICULATA (Nees) or *Karyat.* An Indian plant ; is used as a tonic, and is similar to quassia in its action.

ANDROPOGON OILS v. OILS, ESSENTIAL.

ANDROSIN v. GLUCOSIDES.

ANESIN (*Aneson*). An aqueous solution of acetonechloroform, having marked anæsthetic and hypnotic properties (Apoth. Zeit. 1897, 12, 608) (v. ACETONECHLOROFORM).

ANETHOL v. OILS, ESSENTIAL.

ANGELICA OIL v. OILS, ESSENTIAL.

ANGICO RESIN. A Brazilian gum obtained from *Piptadenia rigida* (Benth.) [*Acacia Angico*]; soluble in water and proof spirit. Used in chest complaints (Symes, Pharm. J. [3] 13, 213). Angico wood is that of another Brazilian leguminous plant, *Enterolobium ellipticum* (Benth).

ANGLESITE. Native lead sulphate ($PbSO_4$), forming brilliant, colourless, orthorhombic crystals, isomorphous with barytes ($BaSO_4$) and celestite ($SrSO_4$). It occurs in the upper oxidised zones of veins of lead ore, having resulted by the alteration of galena (PbS). It is less common than cerussite ($PbCO_3$), with
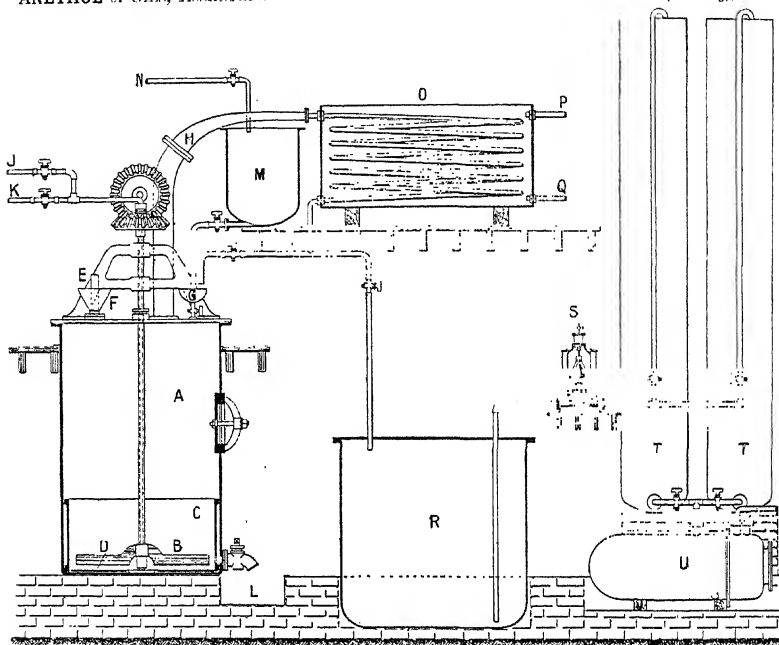
FIG. 1.—ANILINE OIL PLANT.

A, Aniline pan.
B, Agitating blades.
C, Side inlet plates.
D, Bottom do.
E, Wood plug for hopper.
F, Feed hopper for borings.
G, Charging d°.
H, Vapour pipe to condenser.
J, Pure-steam pipe.
K, Aniline-steam do.
L, Gutter.
M, Receiving pan.
N, Pipe from N.B. tank.
O, Condenser.
P, Overflow.
Q, Cold-water inlet.
R, Receiver.
S, Steam pump.
T, Settling tubes.
U, Air pressure egg.

which it has sometimes been mined as an ore of lead. Good crystals have been found at many localities, perhaps most abundantly at Broken Hill, in New South Wales. The mineral takes its name from the Isle of Anglesey, where crystals were found by W. Withering, in 1783, in the Parys copper-mine.   L. J. S.

ANGOSTURA BARK or **ANGUSTURA BARK** v. CUSPARIA BARK.

ANHYDRITE v. CALCIUM.

ANIL. The name of the American species of the indigo plant, *Indigofera anil* (Linn.).

ANILINE.

History.—First observed by Unverdorben in 1826 among the products of the destructive distillation of indigo. Detected by Runge in coal tar in 1834, and by Fritzsche in 1840, among the products obtained by distilling indigo with alkali hydroxides. Prepared by Zinin in 1840, by the reduction of Mitscherlich's nitrobenzene with hydrogen sulphide. Unverdorben called his product *krystallin*; Runge, *kyanol*; Fritzsche, *anilin*; Zinin, *benzidam.*

In 1843 Hofmann showed that nitrobenzene could be reduced by a metal such as zinc in the presence of a dilute acid, and also that krystallin, kyanol, anilin, and benzidam were identical with each other. Shortly afterwards Béchamp stated that nitrobenzene could be reduced by ferrous acetate in the presence of water, but that the oxalate, sulphate, &c., had no effect.

In the year 1856 Perkin's discovery of mauve

gave rise to a commercial demand for aniline, and the manufacture was commenced by Messrs. Simpson & Maule.

Preparation.—Benzene, then only obtained in small quantities and with much difficulty, as the treatment of tar scarcely existed, was introduced into glass balloons (known as 'bolt heads') of 1 gallon capacity, and the calculated quantity of nitric acid, mixed with about an equal volume of sulphuric acid, was gradually added, the mixture swung round and well agitated, and then allowed to stand. It was usual to have about twenty balloons in a row, and to add acid in turn until the reaction was complete.

The nitrobenzene was separated, washed, and reduced with iron borings and acetic acid, at first in a copper still, later in an iron cylinder. The aniline was freed from water, rectified, and was then ready for use. The selling price was about a guinea a pound.

Somewhat later cast-iron cylinders of considerable size were used for the reduction, acetic acid being still used and neutralised with soda or lime at the end of the reaction, and the aniline was in some factories distilled off over a naked fire, in others steam was blown into the mixture, and the aniline and water condensed and separated. Acetic acid continued to be used until about 1866. Since that time the apparatus has undergone little change, the treatment consisting in reduction mainly by the use of iron and water, hydrochloric acid being employed to start the reaction.

The aniline machine shown in Fig. 1 is the type that gives the best results.[1] A careful comparison between this design and the horizontal machine has proved unmistakably that the vertical machine is more economical and better in every respect. This is particularly the case with regard to repairs and maintenance. The machine is of cast-iron, $1\frac{3}{4}$ inches thick, with driving gear, agitating shaft, and blades, as shown in the sketch. An important feature is the renewable cast-iron lining plates at the sides and bottom, which protect the machine from the friction caused by the revolving mass of iron borings. It is 6 feet 6 inches deep, and 4 feet 6 inches in diameter, having a total capacity of 650 gallons. Steam is admitted through the vertical shaft, which is hollow, and passes through the extremities of the horizontal agitating blades. Twenty-one of these machines are required to produce 150 tons of aniline oil per month.[2] A charge of 1000 lbs. of nitrobenzene is run into the receiving pan above the machine. To start the reaction, 1 cwt. of clean cast-iron borings, 10 gallons of hydrochloric acid, and 6 gallons of water are run in through the funnel-shaped hopper, and simultaneously steam is turned on and the nitrobenzene run in a thin stream into the dish on the top of the machine. The wooden plug in the hopper is driven in tight, and the space between it and the hopper is kept full of iron borings. By dexterously manipulating the wood plug, the borings can be added without allowing any vapour to escape. This

simple method of 'feeding' the iron borings has proved better than many of the mechanical feeding devices that have been tried. Distillation proceeds, and the distillate passes through the condenser and runs back into the dish, together with the nitrobenzene which is carried over. The iron borings and nitrobenzene are added only in sufficient quantities to maintain a constant level in the dish. If the reaction proceeds too violently, loss is caused by the formation of benzene. When the level of the liquid in the dish begins to lower, the supply of nitrobenzene and iron borings is increased. This process is continued until the whole charge of nitrobenzene is run in, which takes about 10 hours. The total weight of iron borings required is 9 cwt. A sample caught as it runs from the condenser should then be quite free from nitrobenzene, and the machine will contain only aniline oil, water, and oxide of iron. The supply of steam is then increased, so as to distil over the aniline oil and water,[1] and the distillate is diverted into the tank beneath the condenser. The steam used for this distillation is not pure steam, but is generated from the aniline water mentioned below, in a separate boiler. The aniline water is that which separates from the oil in the separating tubes, and contains about 2 p.c. of aniline oil in solution. The aniline and water in the tank below the condenser are pumped into the settling tubes, and allowed to settle for 48 hours. The distillation of the oil and water from the machine takes about 7 hours, and during the last hour pure steam is again used, so that when the operation is finished, the condensed water left in the machine will be free from aniline, and can be used for flushing out the oxide of iron into the gutter which runs to the settling tanks outside. The oxide, after the water is drained off, is dried and ground, and disposed of for the purification of coal gas from sulphur. Large quantities are also now being used in the manufacture of cheap black paints, and the consumption in this direction is increasing. The aniline oil which has settled to the bottom of the settling tubes is run off into the air-pressure egg below, and blown into the crude aniline-oil store tanks, ready for the final purification by distillation in the vacuum still. The upper layer of water left in the settling tubes, and which contains about 2 p.c. of aniline in solution, is, as already explained, used for feeding the aniline steam boiler. The average yield of crude aniline oil from each machine, with a charge of 1000 lbs. of nitrobenzene, is 765 lbs. The yield of pure aniline oil from nitrobenzene is given further on.

The final purification of the crude aniline oil is done in a vacuum still. The sketch (Fig. 2) shows one of these stills of recent design. The body of the still is wrought-iron, 15 feet long, and 7 feet 6 inches in diameter, having a total capacity of 4000 gallons, and capable of distilling 35,000 lbs. in one charge. The steam is supplied from a boiler having a working pressure of 100 lbs. per sq. inch, at which pressure the steam possesses a temperature of 170°.

[1] See Chem. Trade J. 1906, 38, 59. The writer is indebted to Messrs. Davis Bros. for permission to reproduce the two figures.
[2] Larger machines, on the same principle, in which several tons of nitrobenzene can be reduced, are used by some manufacturers.

[1] In some works this distillation is not done, but the contents of the reduction apparatus are passed immediately through a filter press, the filtrate then running directly or being pumped into the settling tanks.

The internal steam tubes are wrought-iron, 2 inches in diameter. In place of the usual straight tubes which used to be expanded into both end plates, bent tubes are employed, which enter and return to the same end of the still. This prevents the 'tearing' of the tubes owing to expansion and contraction, and the 'breathing' of the end plates. The 'column' is of cast iron, 18 feet high and 9 inches in diameter. The condensing coils consist of three vertical flat copper coils, 2 inches in diameter, arranged side by side in a wrought-iron tank, the distillate entering all the three coils simultaneously from the still head by means of branch pipes. The total length of copper pipe in the

condenser is 432 feet. The two receivers permit continuous working, so that when the first is full, as indicated by the gauge-glass tube, it is shut off, and the second brought into use. The contents of the first can then be drawn off while the second is being filled, and the vacuum is thus maintained throughout.

The still is charged with 35,000 lbs. of crude aniline oil from the store tank, and steam is turned on. The first fraction, about 7 p.c. of the distillate, consists of aniline oil and water, which is added to the crude oil and water in the separating tubes. The next fraction is 'light aniline,' and consists of aniline oil with a small quantity of benzene. If the reduction of the
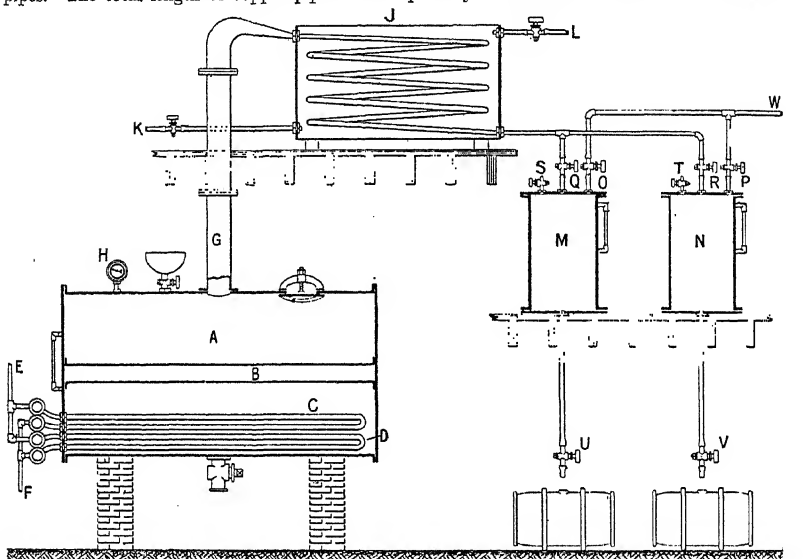
FIG. 2.—VACUUM STILL FOR ANILINE OIL.

A, Vacuum still.	J, Condenser.
B, Internal hollow stay.	K, Cold-water inlet.
C, Steam tubes.	L, Overflow for water.
D, Do. do.	M, Receiver for distilled oil.
E, Steam inlet.	N, Do. do.
F, Do. outlet.	O, Connection from vacuum pump.
G, Vapour pipe to condenser.	P, Do. do. do.
H, Pressure gauge.	Q, Inlet from condenser.

R, Inlet from condenser.	
S, Air-admission tap.	
T, Do. do.	
U, Run-off tap for distilled oil.	
V, Do. do. do.	
W, Connection from vacuum pump.	

nitrobenzene has been carefully performed, this fraction is only about 4 p.c. of the distillate. It is collected and redistilled, giving pure aniline and benzene, the latter being returned to the nitrobenzene department, to be renitrified. The next fraction is pure aniline oil of marketable quality, clear and water-white. The tail end, called 'last runnings,' forms about 5 p.c. of the distillate, and, on redistillation, yields 80 p.c. of pure marketable aniline oil. The total yield of pure aniline oil obtained from nitrobenzene is 71¾ p.c. As the pure benzene yields 154½ p.c. of nitrobenzene, and the latter 71¾ p.c. of pure aniline oil, the total yield of pure aniline oil from pure benzene is 110·85 p.c. Compared with theory, there is little room for improvement.

The process of reduction and rectification as described applies also to toluidine, and modifications of the process are also in use for the production of xylidine and alphanaphthylamine, and of the reduction portion for the manufacture of metaphenylene- and metatolylene-diamine from the respective dinitro- compounds.

Valuation of Commercial Aniline Oil.

Aniline oil, as it occurs in commerce, may contain as impurities water, traces of insoluble hydrocarbons and of orthotoluidine, sometimes traces of hydrogen sulphide, and, if carelessly made, of nitrobenzene, benzene, and ammonia. Besides these, which should be carefully tested for, there is possibly a certain amount of aminothiophen, which has no deleterious action for

most, if not all, of the purposes for which aniline is used, and which, moreover, for the present at least, cannot readily be got rid of.

The method of testing usually adopted is to determine the boiling-point of the sample. For this purpose 100 c.c. are introduced into a small boiling flask with side tube, and distilled through a short condenser into a graduated 100 c.c. cylinder. Readings of the thermometer are taken as each 10 c.c. of the cylinder fills, and the last when 95 c.c. are filled. An alternative method is to take readings of the cylinder at each fifth of a degree rise of the thermometer. It is also usual to note the temperature when the first drop has fallen from the condenser. The thermometer readings should be corrected for barometer and immersion of mercurial column in the vapour of the liquid, and of course for the errors peculiar to the thermometer in use.

A few fragments of platinum wire, fire-brick, or wrought iron, should be placed on the bottom of the flask, and great care used to adjust the size of the flame and rate of boiling. The flask also should be held by the neck in a good clip over the naked flame, gauze being apt to cause currents of heated gas to flow up round the neck of the flask and superheat the vapour.

The specific gravity of the sample may also be taken (pure aniline has a specific gravity of 1·0265–1·0267 at 15°), although this indication is not of great moment if the boiling-points are good.

A recent example of the determination of the boiling-point is the following (Walter, Chem. Zeit. 1910, 34, 702):—

Temperature	P.c. over	Temperature	P.c. over
182·4°	3	183·2°	20
182·6°	4	183·4°	97
182·8°	5·5	183·6°	98
183·0°	11	183·8°	99

Pure aniline may be tested for insoluble oils by dissolving 10 c.c. in 40 c.c. of hydrochloric acid and 50 c.c. of water. The solution should be quite clear.

If, in carrying out the boiling test, the temperature rises considerably at the end, the presence of toluidine may be suspected. This can be detected when a considerable quantity of commercial pure aniline is made into acetanilide. On recrystallising this and working up the mother liquors, a small quantity of impure acetyl compound of low melting-point will always be found in the most soluble portion, or first mother liquors.

Nitrobenzene shows itself with the insoluble hydrocarbons. A very delicate test for it is to shake the sample of aniline violently for a few minutes, and then to notice the colour of the froth. The merest trace of nitrobenzene colours it a very distinct yellow.

The presence of water may be detected by distilling the sample (100 c.c.) as for a boiling-point determination, and collecting the first 10 c.c. in a narrow graduated cylinder of 15 c.c. capacity, shaking with 1 c.c. of saturated sodium chloride solution, and reading off the volume of the latter. The method will not show the presence of less than 0·3 p.c. of water, consequently, 0·3 c.c. must always be added to the amount of salt solution observed. It is not usual for aniline, sold as pure, to contain more than 0·5 p.c. of water.

Toluidine liquid should boil at 197°–198°, show a sp.gr. of about 1·000, and contain 30–40 p.c. para-, the rest ortho- toluidine.

Orthotoluidine. The sp.gr. of commercial orthotoluidine should be about 1·0037; b.p. about 197°–198°; should not solidify on cooling to −4°. Lunge (Chem. Ind. 1885, 8, 74) has published a table showing the specific gravities of mixtures of o- and p-toluidine.

For the estimation of small amounts of p-toluidine in o-toluidine, Schoen's method is perhaps the best. A standard oil is prepared, containing 8 p.c. of p-toluidine and 92 p.c. of o-toluidine, 1 c.c. of which is dissolved with 2 c.c. of pure hydrochloric acid in 50 c.c. of water, and oxidised cold by adding 1 c.c. of a saturated solution of potassium dichromate. After standing for two hours, the product is filtered, the precipitate being washed with water, and the filtrate and washings made up to 100 c.c. The toluidine to be tested is treated in the same manner, and compared colorimetrically with the above solution. J. C. C.

ANILINE BLACK v. DYEING.

ANILINE BLUE v. TRIPHENYLMETHANE COLOURING MATTERS.

ANILINE BROWN v. AZO- COLOURING MATTERS.

ANILINE SALT. The commercial name of aniline hydrochloride $C_6H_5 \cdot NH_2, HCl$.

It is prepared in large quantities for the use of calico-printers, who employ it in the production of aniline black. The process consists in mixing the calculated quantities of pure aniline and hydrochloric acid in lead-lined or nickel-lined tanks, and allowing the salt to crystallise, freeing it from mother liquors in a centrifugal machine, and drying at a low temperature. The hydrochloric acid used should be of good quality, free from iron and even from traces of copper, or the salt will rapidly blacken.

The mother liquors may be neutralised with lime or soda, and the aniline recovered, or they may be boiled down and used in making magenta by the nitrobenzene process, &c.

'Aniline salt' occurs in commerce in large, white, nacreous and much-contorted plates.

The great desiderata for the calico-printer are that the salt should be made from pure aniline and should be dry and normal, containing 93 parts of aniline to 36·5 parts of hydrochloric acid; it should be free from sand and grit, which injure the printing machines.

J. C. C.

ANILINE YELLOW v. AZO- COLOURING MATTERS.

ANIMAL CHARCOAL. (*Noir d'os*, Fr.; *Knochenschwarz*, Ger.) This substance, also known by the name of Bone Black or technically as 'Char,' is formed by carbonising bones at a high temperature in vessels from which air is excluded. Animal charcoal possesses the property of absorbing organic colouring matters from solutions brought in contact with it; thus a solution of brown sugar passed through animal charcoal will be found to have its colour more or less removed. This property is also possessed, though to a far smaller degree, by wood charcoal, as was first noticed by Löwitz about the year 1800. In fact, from that date to 1811, wood charcoal was much employed for

decolourising syrups, but it was then demonstrated by Figuier that bone black was far more effectual and energetic in its action.

In 1812 Louis Constant took out a patent for improving wood charcoal by washing and grinding, and using this prepared charcoal in sugar-refining.

In 1815 Messrs. P. & J. Martineau patented the use of animal charcoal, ' that is to say, animal substances properly burnt, charred, or calcined,' for refining and clarifying sugar; and in 1817 De Cavaillon in a patent, states that he had found that animal charcoal, after it has been used and again calcined, answers for the purpose of bleaching and clarifying sugar in ' a manner superior to new charcoal, and the operation may be repeated any number of times with equal effect.'

In 1830 Charles Derosne described the use of animal charcoal ' reduced to the size of fine gunpowder.' placed on a cloth in a layer to the height of 16 inches, and covered with a perforated diaphragm, as a filter for sugar solutions.

Although the effect of animal charcoal is most conspicuous in removing organic colouring matters from solution, it is also capable of absorbing many other organic and also mineral substances. It was proved by Graham that various mineral substances were removed from solution by animal charcoal; thus the lime is taken up from lime water, and metallic salts are absorbed from their solutions in water. According to Chevallier, lead nitrate and acetate are completely removed by animal charcoal. Weppen has shown that this action extends to a great variety of metallic salts, including cupric, zinc, chromic and ferrous sulphates, nickel, cobalt, silver, mercurous and mercuric nitrates, tartar emetic, stannous chloride, and ferric acetate.

As the result of a number of experiments on the absorption of different salts by animal charcoal, Bodenbender (The Sugar Cane, ii. 316) arrived at the following conclusions:—

1. The power which it possesses of absorbing salts is for the most part a physical property.

2. A given weight absorbs a larger proportion of salts from a concentrated than from a diluted solution; on the other hand, the proportion absorbed from a constant quantity of salts is more considerable when this quantity is in a dilute, than when it is in a concentrated, solution.

3. The presence of sugar has only a slight influence on the absorption of salts.

4. The salts of potassium are retained in smaller proportion than those of sodium.

5. Among the salts experimented with, the amount taken up is in the following order, beginning with that least absorbed: potassium chloride, sodium chloride, potassium nitrate, sodium nitrate, potassium acetate, sodium acetate, potassium sulphate, sodium sulphate, magnesium sulphate, potassium carbonate, sodium carbonate, sodium phosphate.

6. A chemical action of charcoal has been observed with respect to some carbonates, oxalates, and other salts, being brought about by the presence of calcium sulphate and phosphate in the charcoal.

7. Charcoal saturated with one salt is capable, within certain limits, of withdrawing another salt from solution.

8. There is less absorption by charcoal of a salt when in contact with it for a short time, than when the contact is prolonged. The difference due to time of contact, however, ceases when the contact has lasted some hours.

Various explanations have been offered to account for the peculiar action of charcoal. It was attributed by Bussy to the highly divided state of the carbon contained in it. From the similarity of the action of charcoal upon diverse bodies, and the general nature of its operation, it would appear to be due to some physical or mechanical cause. Charcoal seems, indeed, to exert merely a surface action, withdrawing the colour from the liquid passed through it, but not in any way destroying the same, and Kohlrausch has shown by experiment that by means of a solution of ammonia it is possible to practically dissolve out all the colour which has been absorbed by charcoal through which molasses has been previously passed.

In connection with the action of animal charcoal, it is stated by P. Degener and J. Lack (D. R. P. 31358, 1884) that the freshly ignited charcoal, moistened with as much water as it can take up, and exposed to light and air, produces, even in a few minutes, a perceptible quantity of hydrogen peroxide, and is thus rendered more active than the untreated material.

They also state that exposure for 48 hours in layers of 3 inches thick, the charcoal being frequently sprinkled with water and turned over gives good results, and that if milk of lime is sprinkled over bone black, calcium peroxide is produced, and in the same way other alkaline earths and alkalis can be converted into peroxides.

It was first observed by Tilliot that more organic matter is absorbed by charcoal from solutions at a high temperature than in the cold, this result being only partially due to the increased circulation caused by heating.

Manufacture of animal charcoal. The bones employed should be carefully selected, hard, and free from extraneous matter. Whale and fish bones are not of a suitable character, as they yield a soft char. Bones which have been exposed to atmospheric action for a long time, or which have been buried in the ground, cannot be successfully employed, as, owing to the alteration in their composition, they produce a char deficient in carbon.

Before proceeding to carbonise the bones, the fat is removed by boiling, or by means of a suitable solvent such as benzene. By the first-named treatment from 4 to 5 p.c. of fat is extracted, and by the second from 8 to 12 p.c. In the process of extracting fat from bones by means of a solvent, difficulties arise from the presence of water, and F. Seltsam (Eng. Pat. 10208, 1855) has proposed to overcome these by using a solvent (such as a hydrocarbon from petroleum) having a higher boiling-point than that of water, the temperature during extraction being raised to above 100°C. He states that by this means the water is expelled from the bones and the extraction of fat is rendered more complete. Lorenz says that bones after treatment with benzene contain 1·2–2·5 p.c. of fat, which can be extracted by a further treatment with benzene, and 0·48–0·8 p.c. of fat removable by ether, or in all, 1·68–3·3 p.c., which is lost in the process. This mode of extracting fat is employed in many factories on the Continent, and until recently was used in the United Kingdom,

but it is objectionable on the ground that the advantage gained in the increased amount of fat recovered is more than counterbalanced by the decreased value of the resulting animal charcoal.

The apparatus employed in making bone charcoal is similar to that used in a gasworks. The bones are carbonised, after being roughly crushed, in vertical or horizontal iron retorts of a round, oval, or D section, the latter by preference. The length of the horizontal retort is usually from 8 to 10 feet, the long diameter being 18 inches and the short diameter of the oval retort 12 inches. There are usually five or seven retorts in each bed. The retorts are connected in the same way as gas retorts, with a hydraulic main, and this again with condensers or scrubbers filled with coke in which the bone oil separates and from which the gases are exhausted. The gases are then forced through a series of washers containing water to remove the ammonia, the residual gases, which are employed for heating and lighting purposes, finally passing into a gas-holder. Charges of about 2¼ cwt. of bones are carbonised in vertical, and 5 cwt. in horizontal retorts, the operation taking about 6 to 8 hours with the former and 8 to 10 hours with the latter. The bone oil collected in the condenser amounts to from 3 to 5 p.c. on the bones carbonised, and the ammonia in the ammoniacal liquor is equal to about 8 p.c. of ammonium sulphate, into which it is converted in the usual way. When the bones are completely carbonised the charcoal is removed from the retorts and cooled in strong sheet-iron canisters, which are at once covered with closely fitting lids and luted round the edges, either with charcoal paste or a water lute. The char when quite cold is crushed in a suitable mill (on its way to which any iron it may contain is removed by passing over the poles of an electromagnet), and then sifted into various sizes to suit the requirements of the sugar-refiner. It is usually moistened before grinding to keep down the dust. Good bones yield about 65 p.c. of char, but from 20 to 30 p.c. of this is dust, which fetches a lower price than the larger grist.

The following analysis gives approximately the composition of a good sample of new bone charcoal :—

Carbon	.	.	.	.	10·51
Calcium and magnesium phosphates, calcium fluoride, &c.					81·21
Calcium carbonate	.	.	.		7·30
Calcium sulphate	.	.	.		0·17
Ferric oxide	.	.	.		0·12
Silica	.	.	.	.	0·34
Alkaline salts	.	.	.		0·35
					100·00

Moisture originally present . 8·00

Space occupied by one ton, 48 cubic feet.
Sizes left on sieves of various degrees of fineness :—

Above 10 holes to linear inch			.		0
10 to 20	,,	,,	,,	.	28
20 to 30	,,	,,	,,	.	32
30 to 40	,,	,,	,,	.	27
40 to 50	,,	,,	,,	.	11
Through 50	,,	,,	or dust		2
					100

The carbon always contains a certain proportion of nitrogen amounting to about one-tenth of its weight ; there is also a minute proportion of hydrogen present. The nitrogen continually becomes less and less whilst the bone charcoal is being used for sugar-refining.

When char is repeatedly reburned, it becomes less porous and shrinks in volume, so that a ton of char, which, when new, measures 48 to 54 cubic feet, may be reduced to as low as 28 cubic feet after being reburned many times, or, in other words, its apparent density may be nearly doubled.

Wallace has, however, shown that the real sp.gr. varies but little ; thus, a new char occupying 50·6 cubic feet per ton, or having an apparent sp.gr. of 0·71, had a real sp.gr. of 2·822, whilst a moderately old sample, occupying 35 cubic feet per ton, or having an apparent sp.gr. of 1·03, had a real sp.gr. of 2·857, or only a trifle over that of the new.

Another proof that char loses its porosity to a considerable extent by long-continued use and reburning is afforded by the fact, pointed out by Wallace, that dry new char will absorb from 80 to 100 p.c. of its weight of water, whereas old char will only retain from 30 to 45 p.c.

New charcoal of good quality should, in the dry state, contain not less than 9 and not more than 11·5 p.c. of carbon. The silica should not exceed 0·5 p.c., the oxide of iron 0·15 p.c., the calcium sulphate 0·2 p.c., and the moisture 8 p.c. Its weight should not exceed 52 lbs. per cubic foot. It should be of a dull black colour, and, when incinerated, leave an ash of a uniform white or cream colour ; the presence of grey or reddish particles indicates that the sample has been mixed with old charcoal. When brought in contact with the tongue, it should adhere to it somewhat strongly. The size of grain which it is desirable to have in new charcoal depends upon the use to which it is to be applied. Large-grain charcoal is preferable for strong liquors, such as the liquor used for washing loaf sugar. Refiners, as a rule, prefer small grain ; if, however, it be very small, it impedes the passage of liquor and also gives considerable trouble in washing. Char may be used over and over again and sometimes lasts several years, being revivified each time after use by reburning in special kilns (see SUGAR). When, by continued use, it has practically lost its power of removing colour, it is known as spent char, and is then used as a manure, either as it is, or more generally after treatment with sulphuric acid, so as to form superphosphate of lime.

Animal charcoal dust is employed as a pigment after being finely ground either in a dry or wet state ; it is also used in the manufacture of blacking (q.v.).

Ivory black consists of char in an exceedingly fine state of division.

Although the chief use for animal charcoal is in refining sugar, it is also employed for the purification of water, vegetable or mineral oils, paraffin, glycerol, and various other organic substances.

It is sometimes found necessary to use a more powerful decolourising agent than ordinary bone charcoal, and this is prepared by treating new animal charcoal with dilute hydrochloric acid to dissolve out the inorganic constituents,

leaving the carbon behind. This, when carefully washed and dried, forms a most valuable decolourising agent.   N. BROS.

ANIMAL OILS and **FATS** *v.* OILS AND FATS.

ANIME and **ANIMI** *v.* OLEO-RESINS.

ANISEED. (*Anis*, Fr., Ger.) The fruit of the *Pimpinella Anisum* (Linn.), cultivated in Malta, Spain, and Germany. Used for the preparation of anise oil and cordials. Alcohol extracts 36·24 p.c. of this spice (Biechele, Pharm. J. [3] 10, 878).

ANISE CAMPHOR *v.* CAMPHORS.

ANISE OIL. The essential oil of aniseed, obtained by distilling it with water. According to Landolph (Compt. rend. 81, 97 ; 82, 226), it contains 90 p.c. of *anethole*, boiling at 226°. Anethole, according to Perkin (Chem. Soc. Trans. 32, 668), is *p*-allylanisole $C_6H_4(OMe)CH : CH·CH_3$; he obtained it by heating *p*-methoxyphenylcrotonic acid.

Anise oil is sometimes adulterated with fennel oil ; this can be detected by heating the oil, when the fennel odour becomes perceptible.

Star anise oil has a similar colour and taste, but it does not solidify at 2° (*v.* OILS, ESSENTIAL).

ANISIDINE. $NH_2·C_6H_4·OMe$. *Orthanisidine.* Obtained by the reduction of orthonitranisole with tin and hydrochloric acid or iron and hydrochloric acid (Meister, Lucius, and Bruning, D. R. P. 7217 of Dec. 3, 1878), is a colourless oil, which boils at 226·5° at 734 mm. pressure (Mühlhaüser, Annalen, 207, 239) ; at 225° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210), and has a sp.gr. 1·108 at 26°. When diazotised and treated with β-naphtholdisulphonic acid (R-acid), it yields *anisole-red* (*v.* AZO- COLOURING MATTERS). A mixture of orthanisidine (2 mols.) and paraphenylenediamine (1 mol.) is converted, on oxidation with potassium dichromate, into a reddish colouring matter formerly employed under the name *safranisole* (Kalle & Co., D. R. P. 24229 of Oct. 27, 1882 ; expired March, 1885).

Paranisidine, obtained from paranitranisole by reduction with tin and hydrochloric acid, crystallises in prisms which melt at 55·5°–56·5° (Lossen, Annalen, 175, 324) and boil at 245°–246° (Salkowski, Ber. 7, 1009) ; 243° at 760 mm. (Perkin, Chem. Soc. Trans. 69, 1210) ; *p*-anisidine, *o*-sulphonic acid, prepared by boiling the hydrogen sulphate of *p*-anisidine, when diazotised and coupled with β-naphthol, yields an azo-compound forming red lakes with baryta, alumina, &c. (Aktiengesellschaft für Anilin-Fabrikation, D. R. P. 14665).

Chloranisidine, when diazotised and coupled with β-naphthol, yields a red compound insoluble in water (Julius, Ludwigshafen and Jahrmaht, U.S. Pat. 695812) ; *p*- and *m*-nitroanisidine, when diazotised and coupled with β-naphthol, yield red and pink dyestuffs (Imray, Eng. Pat. 25756; J. Soc. Chem. Ind. 1898, 1039 ; and Freyss, J. Soc. Chem. Ind. 1901, 356) ; *o*-iodo-*p*-anisidine, when diazotised and treated with naphthol sulphonic acid, yields a red dye, similar to that obtained from *p*-anisidine (Reverdin, Ber. 29, 997).

Anisidine condenses with orthoformic ester, and the resulting compound is used as an anæsthetic (Goldchsmidt, Eng. Pat. 9792 ; J. Soc. Chem. Ind. 1899, 606).

ANISOCHILUS CARNOSUS (Wall.). An

Indian plant belonging to the Labiatæ and containing a volatile oil. Used in quinsy.

ANISOLE. *Anisoil ; Methylphenyl ether* $C_6H_5·O·CH_3$.

Preparation.—Anisole can be obtained by distilling anisic acid or *o*-methoxybenzoic acid with baryta, or by heating potassium phenate with methyl iodide at 120° (Cahours, Ann. Chim. Phys. [3] 2, 274 ; 10, 353 ; 27, 439). It is prepared by passing a current of methyl chloride over dry sodium phenate heated at 190°–200° (Vincent, Bull. Soc. Chim. 40, 106), and by heating phenol with methyl alcohol and potassium bisulphate at 150°–160° (Act. Ges. für Anil.-Fabrik.; D. R. P. 23775). It has been synthesised by fusing sodium benzene sulphonate with sodium methoxide (Moureu, J. Pharm. Chim. 8, v. 211).

Properties.—It is a colourless ethereal liquid, which boils at 155°–155·5° at 762·3 mm. (Schiff, Annalen, 220, 105) at 153·9° (corr.) (Perkin, Chem. Soc. Trans. 69, 1240) ; melts at − 37·8° (Von Schneider, Zeit. Phys. Chem. 19, 997) and has a specific gravity 0·991 at 15° (*v.* OILS, ESSENTIAL).

ANISOMELES MALABARICA (R. Br.). A much-esteemed Indian plant belonging to the Labiatæ ; an infusion of the leaves is used in intermittent fevers, and the essential oil is applied externally in rheumatism.

ANKOOL, AKOLA, DHERA BARK. The root bark of *Alangium Lamarckii* (Thw.), one of the Cornaceæ, used in leprosy and skin-diseases (Dymock, Pharm. J. [3] 9, 1017).

ANNATTO is derived from the fruit of the *Bixa orellana* (Linn.), a shrub found native in Central America, and cultivated in Brazil, Guiana, Mexico, the Antilles, and India.

To prepare the dyestuff, the seeds and pulp are removed from the mature fruit, macerated with water, and the mixture is left to ferment. The product is strained through a sieve, and the colouring matter which settles out is collected, partially evaporated by heat, then placed in boxes, and finally dried in the sun.

Annatto comes into the market in the form of cakes, and, among the different varieties, Cayenne annatto is the most esteemed, and is considered to be the richest in colouring matter. It should contain from 10 to 12 p.c. of the pure dye, and not more than 5 p.c. of ash, whereas the amount of colouring matter in the Bengal product is frequently lower than 6 p.c.

In 1848 Dumontal devised a new method for the preparation of annatto, in which fermentation is avoided, and the pulp is simply washed out from the capsules and off the seeds. The product known as *bixin* is said to be five to six times more valuable than ordinary annatto (Crookes, Dyeing and Calico-Printing).

The colouring matters of this dyestuff were first investigated by Chevreul (Leçons de chimie appliquée à la Teinture), who isolated two substances, one yellow, which was called *orcelline*, soluble in water, and a second, *bixin*, which is red and very sparingly soluble.

Bixin, the useful colouring matter, was subsequently examined by numerous chemists, who were only successful in preparing it as an amorphous powder, and its isolation in a crystalline condition was first achieved by Etti (Ber. 7, 446 ; 11, 864).

Etti digested 1·5 kilos of purified annatto

with a solution of 150 grams of calcined soda ash in 2·5 kilos. of 80 p.c. alcohol on the water-bath at 80°. The mixture was filtered and the residue pressed between warm plates, and again extracted with 1·5 kilos. of warm 60 p.c. alcohol.

The alcoholic filtrate was diluted with half its volume of water, concentrated sodium carbonate solution added, and the crystalline precipitate of sodium bixin was collected after several days, and pressed. The product purified by solution in 60 p.c. alcohol at 70°–80°, and reprecipitation with sodium carbonate was finally made into a cream with alcohol, and this, when neutralised with hydrochloric acid yielded crystalline bixin.

A simpler method has been more recently devised by Zwick (Ber. 30, 1972). Well-dried annatto is extracted for 24 hours with boiling chloroform, the extract evaporated, and the residue thoroughly exhausted with ligroin. The product is crystallised from chloroform, and after washing with ligroin, is repeatedly recrystallised from the former solvent.

Bixin $C_{28}H_{34}O_5$ (Etti, *l.c.*; Marchlewski and Matejko, Chem. Zentr. 1906, ii. 1265) consists of brown-red or deep-red rhombic crystals, which, when slowly heated, melt at 191·5°, and when rapidly heated, at 198°. It is sparingly soluble in the usual solvents, and of these it is most readily dissolved by chloroform or alcohol. Concentrated sulphuric acid dissolves bixin with a cornflower-blue colouration, and this reaction is characteristic, and is given by minute traces of the substance.

Monosodium bixin $C_{28}H_{33}O_5Na+2H_2O$ is best prepared by dissolving 10 grams of bixin in a solution of 1·2 grams of sodium carbonate in 300 c.c. of 12 p.c. alcohol at 70° (Etti, Zwick). It is deposited on cooling in dark-red iridescent crystals, and can be obtained in the anhydrous condition by recrystallisation from 70 p.c. alcohol (M. and M.).

Disodium bixin $C_{28}H_{32}O_5Na_2+2H_2O$ is obtained when 20 grams of bixin is dissolved in a solution of 10 grams sodium carbonate in 600 c.c. of boiling 12 p.c. alcohol. It consists of a dark-red amorphous powder (Etti). *Monopotassium bixin* $C_{28}H_{33}O_5K+2H_2O$ and *dipotassium bixin*, $C_{28}H_{32}O_5K_2+2H_2O$ have also been prepared.

Bixin contains one methoxyl group. Distilled with zinc-dust, bixin yields, according to Etti, *metaxylene*, *metaethylxylene*, and a hydrocarbon $C_{14}H_{14}$, b.p. 270°–280°.

According to Zwick, bixin is readily reduced by sodium amalgam, and a compound, $C_{23}H_{40}O_7$, is thus produced. Marchlewski and Matejko, on the other hand, studied the action of zinc-dust and acetic acid, and obtained in this manner an orange-coloured crystalline substance which possessed a strong metallic lustre. When slowly heated, it melts at 200·5°, but if the operation is carried out rapidly, at 208°–210°. This compound is evidently of an unstable nature, for whereas when freshly prepared it gives C=75·4, H=7·7 p.c., on standing for some days in the air it becomes colourless and then gives C=58·6, H=5·8 per cent. At 100° this change occurs more rapidly.

Dyeing properties.—Annatto is still employed to a fair extent for colouring oils and butter, but is almost extinct as a dyestuff in this country. As the orange-red colour which it yields is extremely fugitive to light it has at no time been very extensively used. On the other hand, it resists the action of soap and dilute acids very well.

In order to dye cotton, the annatto is first dissolved in a boiling solution of carbonate of soda, and the goods are then entered and left in the bath for a quarter of an hour. They are subsequently pressed out, and washed in slightly acidulated water or alum solution.

For silk, the bath is made up with equal parts of annatto and sodium carbonate; soap is also usually added, and the dyeing is continued at 50° for about an hour, according to the shade required. The colour produced can be rendered somewhat more yellow by passing the fabric through a weak solution of tartaric acid.

Wool is dyed at 80°–100°, without any addition to the bath. A. G. P.

ANNEALING. (*Le recuit*, Fr.; *das Anlassen*, Ger.) A process which is applied principally to glass and metals for the purpose of rendering them softer or less brittle. The process itself always consists in the application of heat for a period of time, which may vary from a few minutes to many hours, and which may be followed by very slow cooling; the object of the process is to permit the material to attain approximate equilibrium in regard to its internal structure. This state of normal internal equilibrium may be disturbed either by the effects of rapid cooling or by the application of mechanical deformation. The former is most frequently met with in glass, and in large metal castings, while the latter is found in ' wrought ' metal of all kinds.

In the case of substances which are poor conductors of heat, such as glass, and also in masses of metal which are so large that thermal conductivity cannot produce reasonable uniformity of temperature, relatively rapid cooling sets up severe stresses, owing to the fact that the outer or most rapidly cooled layers solidify first; subsequently the internal portions of the mass endeavour to contract in solidifying, and in cooling, but find themselves constrained by their attachment to a relatively rigid external envelope; the tendency to thermal contraction is therefore overcome by severe tensional stresses. A body in this condition, while it may present the phenomenal strength of a ' Rupert's drop,' is liable to sudden fracture, particularly if the surface is cut or broken. In such substances, effective annealing implies heating to a point where the mass becomes sufficiently soft to release all internal stresses, followed by very slow cooling down to the temperature at which the body is completely solid. In the case of fine optical glass, the rate of cooling is retarded so that a fall of 100° occupies one week. For metals such excessively slow cooling is undesirable, and is never intentionally used.

Metals in the cast or other ' normal ' condition consist of aggregates of minute crystals of approximately equal dimensions in all directions; when metal is mechanically deformed, as by hammering, rolling, or other working process carried on in the cold, these minute crystals are elongated in the same general sense as the mass of which they form part, and this

deformation of the crystals is accompanied by the well-known hardening of the metal under cold work. This is due in part to the internal rearrangement which each crystal undergoes, and in part to the partial and local destruction of the crystalline arrangement itself, accompanied by the formation of a hard amorphous 'phase' (Ewing and Rosenhain, Phil. Trans. 1899, ser. A, cxiii. 353–375; Beilby, Phil. Mag. 1894). When the metal is subsequently annealed, *i.e.* heated to a suitable temperature, the metal 'recrystallises,' the crystals rearrange themselves, and the original condition is approximately restored. In some metals the molecular mobility is such that recrystallisation takes place slowly even at the ordinary temperature (lead: Ewing and Rosenhain, Phil. Trans. 1900, cxcv. 279–301; brass: Cohen, Rev. general des Sciences, April 30, 1910); but in the greater number of cases a high temperature is required. In the great majority of pure metals, and in some alloys, the rate of subsequent cooling is immaterial so far as the softening effect is concerned; but in certain metals and in a large number of alloys either allotropic or other changes take place during gradual cooling, and these transformations are more or less inhibited by rapid cooling; in such metals the rate of cooling through the 'critical temperatures' at which these changes occur is of material importance. The most striking example is found in carbon steels, which are moderately soft if cooled slowly down to a temperature of 650°, but become exceedingly hard if suddenly cooled from a temperature above 700°. In the case of hardened tool steel, the process of annealing consists in raising the steel to such a temperature (above 700°) that the changes which were suppressed when the steel was hardened by quenching are allowed to take place during the heating and cooling process.

In many metals the annealing process is liable to be complicated by the effects of chemical actions between the metal and its solid or gaseous surroundings, as well as by the effects of the growth of the constituent crystals of the metal; at high temperatures these crystals tend to increase in size, and the resulting coarsening of the grain of the metal leads to a deterioration in mechanical properties. Annealing at an unduly high temperature or for too long a time thus becomes 'over-heating,' and is injurious to almost all metals and alloys, notably to steel and brass. W. R.

ANODYNINE. Identical with antipyrine (*q.v.*).

ANONA MURICATA (Linn.). A decoction of the root is used as an antidote for fish-poisoning, and the bark serves as an astringent. The leaves are useful in softening abscesses, and from the seeds a wine can be prepared which is said to be beneficial in cases of diarrhœa (Chem. Zeit. 10, 433; J. Soc. Chem. Ind. 5, 332).

ANORTHITE *v.* FELSPAR.

ANOZOL. Trade name for a preparation of iodoform deodorised by 10–20 p.c. of thymol.

ANTHEMOL *v.* CAMPHORS.

ANTHIONE. Trade name for a solution of potassium persulphate. Employed as a photographic reagent.

ANTHOKIRRIN. The yellow crystalline matter of the flowers of the yellow toadflax (*Linaria vulgaris*). Formerly used as a dyeing material, but the colour is not permanent.

ANTHOKYAN. The expressed juice of the sweet or purple violet (*Viola odorata*), gently heated to 89°, then skimmed, cooled, and filtered. A little rectified spirit is then added, and the following day the whole is again filtered. Used to make syrup of violets, and to colour and flavour liqueurs.

ANTHOPHACIN. A term given by Möbius (Chem. Zentr. 1901, i. 190) to the brown colouring matter of flowers.

ANTHRACENE $C_{14}H_{10}$. Discovered by Dumas and Laurent in the highest boiling portion of coal tar, and termed by them *paranaphthalene* (Annalen, 5, 10); further examined by Laurent, who re-named it *anthracene* (Annalen, 34, 287); first obtained pure, and its composition determined, by Fritzsche (Annalen, 109, 249), and more exactly studied by Anderson (Annalen, 122, 294; Chem. Soc. Trans. 15, 44).

Occurrence.—Anthracene is one of the products of the destructive distillation of coal, and is found in the tar; the average yield of the pure hydrocarbon is about 0·3 p.c. of the tar obtained.

A new source of anthracene has been announced (Dingl. poly. J. 246, 429) in the tar obtained when the residue, left after the illuminating oils have been distilled from Baku petroleum, is allowed to fall on pumice in red-hot iron retorts. 1000 kilos of naphtha residue under these conditions yield 500 c.m. of gas, used to heat the retorts, and 300 kilos. of tar, containing about 0·2 p.c. of pure anthracene. The supply of the naphtha residue is, however, too limited to render anthracene from this source a serious competitor with that from coal tar.

According to Elliott (Amer. Chem. J. 6, 248), the tar obtained in the manufacture of gas by the destructive distillation of light petroleum naphtha boiling below 150° contains 2·63–2·90 p.c. of anthracene. A remarkable production of anthracene, during the distillation of the higher-boiling portions of crude phenol, has been observed by Köhler (Ber. 18, 859).

Anthracene is obtained by the distillation of rhein with zinc-dust (Oesterle and Tesza, Arch. Pharm. 1908, 432), but this production is of no commercial value.

Preparation (Auerbach, Das Anthracen und seine Derivate; Kopp, J. 1878, 1187; Perkin, Journ. Soc. Arts, 27, 572; Lunge, Coal Tar and Ammonia).—Anthracene is obtained from the 'green grease' which forms the last portion of the 'heavy oil' or 'dead oil' of the tar distiller; this at first is a brown liquid with a green fluorescence, but soon becomes semi-solid on standing, owing to the separation of solid substances. When no further separation occurs, the mass is subjected to filtration, either in a centrifugal machine or a filter press, first in the cold and finally at 40° (Gessert, Dingl. poly. J. 196, 543); or is filtered through strong linen bags, and afterwards submitted to hydraulic pressure in a press so arranged that the plates can be heated with steam and the cake hot-pressed. A notable quantity of anthracene remains dissolved in the expressed oil, and especially in the portions separated when the temperature is raised, and is recovered by redistilling and

working up the product as just described. The hard yellowish-green cake obtained, containing 25–40 p.c. of pure anthracene, is ground to a fine powder in mills and heated with coal-tar naphtha (b.p. 80°–100°), solvent naphtha (b.p. 120°–190°), creosote oil, or petroleum spirit (b.p. 70°–100°), in large iron vessels provided with stirrers. Petroleum spirit is to be preferred (Perkin), since it dissolves less anthracene whilst the impurities are sufficiently soluble in it to be removed if the quantity of solvent employed is 2–3 times as great as that of the anthracene to be purified. Solvent naphtha, consisting essentially of xylenes, pseudo-cumene and mesitylene, is extensively employed, as phenanthrene is much more soluble than anthracene in this solvent. When creosote oil is used, it must be free from naphthalene; the advantage of using creosote oil is that it dissolves out the methyl anthracene, the anthracene being practically insoluble therein. The residue contains from 45–50 p.c. of the hydrocarbon, but inasmuch as it is not readily reduced to powder, and unless finely divided is only slowly attacked by oxidising agents, it is sublimed by passing steam, heated at 220°–240°, over the melted product, and condensing the vapours in a chamber by jets of water. The anthracene thus obtained is in leafy masses, containing from 50–60 p.c. of the hydrocarbon, the chief impurities consisting of carbazole (10–12 p.c.), phenanthrene, pyrene, chrysene, and other hydrocarbons, together with small quantities of phenols of high boiling-point, and of acridine; it can readily be ground to a paste, and is now sufficiently pure for conversion into anthraquinone by oxidation. If, however, dichloranthracene is required, further purification is necessary; this can be effected by distillation with caustic potash, whereby impurities such as carbazole and bodies of a phenolic character are retained, and anthracene, together with phenanthrene, distils over with no greater loss than occurs if the 60 p.c. product is distilled alone; caustic soda cannot be substituted for the potash, since it produces no purification of any consequence. Instead of distilling washed anthracene (100 parts) with caustic potash, Perkin employs a mixture of Montreal potash (30 parts), which usually contains potassium hydroxide in considerable quantities, and caustic lime (6 parts). Unless lime is used, the residue in the retorts forms a hard cake, which can be removed only with difficulty. Hydrogen is evolved during the distillation. The distillate is freed from phenanthrene by washing with coal-tar naphtha, and the residue is a very pure anthracene. This production of phenanthrene, even from anthracene which has been freed from this impurity by extraction with solvents previous to distillation with caustic potash, is noteworthy and points to the probable existence of molecular compounds of phenanthrene with other of the impurities of the washed anthracene, which are destroyed during the distillation with caustic potash. This process of Perkin has been subjected to considerable criticism. According to Auerbach, a loss of anthracene to the extent of 10 p.c. occurs, and this, added to the cost of fuel employed, renders it the most costly method of purification yet devised. The great advantage of the method, however, is that it brings anthracenes

of different origins to a similar condition of purity; even pitch anthracene—obtained by the distillation of gas-tar pitch in iron retorts with the aid of super-heated steam, and generally unsuitable for purification owing to the difficulty of removing higher hydrocarbons associated with it—works perfectly well after it has been subjected to this process.

Many modifications in the method of purifying crude anthracene have been introduced. A method based on the far greater solubility of the impurities in mixtures of aniline, pyridine, or quinoline bases, has been patented by the Chemische Fabriks-Actiengesellschaft in Hamburg (D. R. P. 42053 of April 15, 1887). The crude anthracene is dissolved at 100° in 1½–2 times its weight of a dehydrated and rectified mixture of tar bases (pyridines) separated from the light oil obtained in tar distillation (compare D. R. P. 34947 and 36372), and the solution, on cooling, yields a crystalline separation of anthracene almost free from carbazole and its homologues. The patentees state that a 33 p.c. anthracene dissolved in 1·75 times its weight of pyridine bases yields on crystallisation an 82·5 p.c. anthracene, whilst when dissolved in twice its weight of a mixture of equal parts of pyridine bases and benzene, it yields an 80 p.c. anthracene, and in twice its weight of a mixture of equal parts of benzene and aniline a 75 p.c. anthracene. The recovery of the anthracene contained in the mother liquors offers no special difficulty.

Remy and Erhart (D. R. P. 38417 of Jan. 19, 1886) have proposed crystallisation from oleic acid as a means of purification of crude anthracene. The difficulty of recovering the anthracene contained in the mother liquors would seem, however, to deprive this method of technical importance.

Graham (Chem. News, 33, 99, 168) has devised a method for recovering anthracene from the filtered oils used in its purification.

The Farbenfabriken vorm. Friedr. Baeyer & Co. (D. R. P. 68474; Eng. Pat. 5539; J. Soc. Chem. Ind. 1893, 439) employ liquid sulphur dioxide, which dissolves the impurities of crude anthracene, but very little anthracene itself. 600 kilos. crude anthracene is mixed in a wrought iron agitator with 2400 kilos. liquid sulphur dioxide, first exhausting the air and then allowing the sulphur dioxide to enter. The reaction having ceased, the mass is forced by its own vapour pressure into an iron steam-jacketed, filtering tower, where anthracene of 70–80 p.c. remains behind. The mother liquor is distilled, the sulphur dioxide being collected and recondensed by means of an air-compressor.

Another patent of the same firm (D. R. P. 77861; Eng. Pat. 7862; J. Soc. Chem. Ind. 1895, 361) recommends the use of acetone or other fatty ketones as a purifying agent. 560 kilos. crude anthracene is stirred in a steam-jacketed cylinder with 750 kilos. acetone for an hour. After cooling the separated anthracene is filtered and washed with 375 kilos. acetone. The second liquor is used over again, and the first is distilled to recover the acetone. From crude stuff containing 34 or 35 p.c. anthracene, an article of 82 p.c. is easily made, and only a few per cent. anthracene remain in the residue after distilling off the acetone. The acetone may be

used in the form of 'raw acetone' or 'acetone oils.'

Welton (Eng. Pat. 27559; D. R. P. 113291; J. Soc. Chem. Ind. 1900, 139) purifies crude anthracene by means of liquid (anhydrous) ammonia, which dissolves out most of the impurities, but not the anthracene itself.

Luyten and Blumer (Eng. Pat. 14892; D. R. P. 141186; J. Soc. Chem. Ind. 1901, 796) state that when anthracene is purified by solvents such as naphtha, acetone, &c., the presence of tar oil in the crude anthracene is beneficial. 25 parts of drained crude anthracene are heated with 35 parts of naphtha until the temperature is near that of the solvent. On cooling, the anthracene crystallises out and is filtered and washed with a little of the solvent. It is dried by heating to fusion, and distilling off the solvent; 80 p.c. anthracene is obtained by this method.

The Aktien Gesellschaft für Theer und Erdöl Industrie (D. R. P. 111359; Eng. Pat. 7868; J. Soc. Chem. Ind. 1899, 750) heat crude anthracene to fusion, and allow it to cool until 50 p.c. has crystallised, when the mother liquor is run off and again allowed to crystallise. The second crop can be raised to the value of the first (45–50 p.c.) by another fusion. This product is again fused and treated with caustic potash lye (50 p.c.) in quantity sufficient to react with the carbazole present. When the reaction is complete, the mass separates into two layers, the lower part being potassium carbazole. The upper anthracene layer is run into its own volume of 90's benzol, which dissolves any phenanthrene. The anthracene is pressed or centrifuged, and again washed with the same solvent, and is obtained as a pale-brown powder. By this means 30 p.c. anthracene is raised to 90 p.c. (v. also Scholvien, Fr. Pat. 335013; J. Soc. Chem. Ind. 1904, 113).

The Aktien Gesellschaft fur Anilinfabrik (D. R. P. 178764; J Soc. Chem. Ind. 1907, 1193) add potassium hydroxide to the melted crude anthracene, which is then distilled in vacuô, the anthracene distilling over being passed into some solvent in which it is soluble at the temperature of the reaction, and from which it crystallises on cooling. It is stated that 95–96 p.c. of the anthracene is recovered as a product containing 95–98 p.c. of pure anthracene.

Wirth (Eng. Pat. 14462; J. Soc. Chem. Ind. 1901, 464) separates the carbazole by means of its easily soluble nitroso- compound. Crude anthracene is mixed in a vessel provided with a stirrer with light coal-tar oil and sodium nitrite. Dilute sulphuric acid is added gradually, and the sodium sulphate which is formed is dissolved in water and separated from the light-oil layer. The anthracene is filtered from the light coal-tar oil, washed with benzene, and dried. It contains 75–95 p.c. anthracene, according to quality of the crude material.

Catchpole (Eng. Pat. 16641; D. R. P. 164508; J. Soc. Chem. Ind. 1903, 1190) places the crude product in the form of blocks or slabs on a perforated or channelled surface in a chamber suitably heated to a temperature not exceeding 200°, whereby the impurities are 'sweated' out. A slight washing with acid and distillation complete the process.

Vesely and Votocek (Eng. Pat. 27596; J. Soc. Chem. Ind. 1905, 191) find that concentrated sulphuric acid extracts the whole of the basic impurities of anthracene from a solution of crude anthracene in a solvent immiscible with sulphuric acid. The most suitable solvents are mineral and coal-tar oils, but carbon disulphide and chloroform may be used; 100 parts of crude anthracene (35 p.c.) are dissolved in 300 parts of solvent naphtha, 100 parts of concentrated sulphuric acid are added, and the mixture is heated and at the same time vigorously agitated for a few minutes. The sulphuric acid having been drawn off, the solution is freed from acid by agitation with calcium carbonate, filtered, and then allowed to crystallise. By this process it is stated to be possible to obtain an 85–90 p.c. anthracene, perfectly free from carbazole.

A troublesome impurity in anthracene is a peculiar paraffin, which has a high melting-point, and is only sparingly soluble either in light petroleum or coal-tar naphtha; it is dissolved to a certain extent by these solvents when hot, but on cooling is almost entirely deposited again. A small quantity left in the anthracene frequently impedes succeeding operations, and, owing to its stability, passes through most of the processes without change.

Syntheses.—From orthotolylketone, by heating with zinc-dust (Behr and Van Dorp, Ber. 7, 17); from orthobenzylbromide, by the action of sodium (Jackson and White, Ber. 12, 1965); from a mixture of benzene, acetylene tetrabromide, and aluminium chloride (Anschütz, Annalen, 235, 156); from benzene and aluminium chloride under the influence of nickel carbonyl at 100° (Dewar and Jones, Chem. Soc. Trans. 1904, 213); and by treating pentachlorethane in benzene with aluminium chloride, when anthracene is formed through the intermediate formation of perchlorethylene (Mouneyrat, Bull. Soc. chim. 19, [3] 557). An interesting synthesis resulting in the production of methyl anthracene (m.p. 200°) is that of Kraemer and Spilker (Ber. 1890, 3174). By the interaction of xylene and cinnamene, phenyltolylpentane is formed, which when passed through a red-hot tube forms methyl anthracene (m.p. 207°), hydrogen and methane being evolved. This synthetical production of methyl anthracene is of importance in its relation to the present theories of the mode of formation of anthracene in coal tar.

Properties.—Anthracene crystallises in glistening white scales. It melts at 216·5° (Reissert, Ber. 1890, 2245), and boils at 382° (Schweitzer, Annalen, 264, 193). When pure, it shows a bluish-violet fluorescence, but this is concealed if small quantities of yellow impurities (Fritzsche's chrysogen) are present. Yellow-coloured anthracene, on exposure to sunlight, is bleached, and becomes fluorescent, but under these conditions the hydrocarbon undergoes conversion into paranthracene $(C_{14}H_{10})_2$—a peculiar modification, which is much less soluble than anthracene, is unattacked by bromine and nitric acid at 100°, and does not combine with picric acid; it melts at 244°, and is thereby converted into ordinary anthracene (Fritzsche, J. pr. Chem. 101, 333; Graebe and Liebermann, Annalen, Suppl. 7, 264;

Schmidt, J. pr. Chem. [2] 9, 248). The fluor-escence of anthracene and certain of its deriva-tives has been referred by Liebermann to a particular molecular grouping (Ber. 13, 913). Meyer (Zeitsch. physikal. Chem. 1897, 468) attributes fluorescence to the presence of what are known as fluorphoric groups, which must be situated between two heavy atomic groups, usually benzene nuclei. The solubility of anthracene in 100 parts of various solvents has been determined by Versmann (Jahresbericht. 1874, 423), Perkin (Journ. Soc. Arts, 27, 598 : v. Becchi, Ber. 12, 1978), Findlay (Chem. Soc. Trans. 1902, 1221) with the following results :—

	Parts of anthracene
Alcohol (absolute) at 16° dissolves	0·076 (B.).
,, b.p.	0·830 (B.).
,, sp.gr. =0·800 at 15°	0·591 (V.).
=0·825 ,,	0·574 (V.).
=0·830	0·491 (V.).
=0·835	0·475 (V.).
=0·840	0·460 (V.).
=0·850	0·423 (V.).
Ether	1·175 (V.).
Chloroform	1·736 (V.).
Carbon disulphide	1·478 (V.).
Acetic acid	0·444 (V.).
Light petroleum .	0·394 (V.).
,, . b.p. 70°–100° at 15° dissolves	0·115 (P.).
Benzene .	1·296 (F.).
,, b.p. 80°–100°	0·976 (P.).
Toluene . . at 16·5°	0·920 (B.).
,, . . at b.p.	12·940 (B.).

When introduced into an alcoholic solution of picric acid saturated at 30°–40°, anthracene forms a picrate $C_{14}H_{10},C_6H_3(NO_2)_3O$, crystal-lising in glistening red needles which melt at 138°; it is decomposed into its constituents by alcohol, water, and dilute alkalis, even in the cold. The formation of the picrate is best obtained by warming molecular quantities of anthracene and picric acid on the water-bath in chloroform solution. On oxidation with po-tassium dichromate or manganese dioxide and sulphuric acid, anthracene is converted into anthraquinone, whilst strong nitric acid oxidises it to anthraquinone and dinitroanthraquinone ; nitro- derivatives of anthracene can, however, be prepared by the action of strong nitric acid on the hydrocarbon, if care is taken to decompose any nitrous acid which may be formed during the reaction (Perkin, Chem. Soc. Proc. 1889, 13). Electrolytic oxidation in acetone yields anthra-quinone (Fontana and Perkin, Chem. Zentr. 1904, ii. 708); the same product results by the electrolytic oxidation of a suspension of anthra-cene in a 2 p.c. solution of cerium sulphate in 20 p.c. sulphuric acid at 80°–90° (Farb. vorm. Meister, Lucius and Bruning, D. R. P. 152063 ; Chem. Zentr. 1904, ii. 71) ; or by the oxidation of anthracene by cerium oxide in sulphuric acid (Farb. M. L. & B.; D. R. P. 158609; Chem. Zentr. 1905, i. 840) ; or by heating anthracene with charcoal at 150°–300° (Dennstedt and Hassler, D. R. P. 203848 ; Chem. Zentr. 1908, ii. 1750).

Concentrated sulphuric acid converts anthra-cene into sulphonic acids. Anthracene mono-sulphonic acid is obtained by the direct sulphona-tion of anthracene with sulphuric acid of 53° or 54°B., and about 60 p.c. of the anthracene employed is thus converted. If sulphuric acid of 66°B. is used, two isomeric disulphonic acids are obtained, and these, on oxidation, yield two anthraquinonedisulphonic acids, which are isomeric with the two acids obtained by the direct sulphonation of anthraquinone. The β-anthracene disulphonic acid, after oxidation with chromic or nitric acids, and subsequent fusion with alkali, yields *alizarin* (q.v.), and the monosulphonic acid similarly treated yields *anthrapurpurin* (q.v.) (La Société Anonomye des Matières Colorantes et Produits Chemiques de St. Denis, Eng. Pat. 1280 ; J. Soc. Chem. Ind. 1894, 32).

The same acids are obtained by heating anthracene with alkali bisulphate to 140°–150° (D. R. P. 77311). Anthracene is readily attacked by chlorine and bromine, and yields with each element a series of additive and substitution derivatives ; additive compounds, apparently, are the first products of the action, and these either decompose during the reaction or can be decomposed by boiling with alcoholic potash into the corresponding substitution derivatives, which also form additive compounds by the further action of the halogens. The chloranthra-cenes are now prepared on a large scale (Clayton Aniline Co., Eng. Pat. 8744 ; J. Soc. Chem. Ind. 1906, 64). Dry chlorine reacts with anthracene in the presence of lead peroxide at a high temperature. Fifty parts by weight of anthracene and 10 parts of dry powdered lead peroxide are treated with dry chlorine at 220° until the weight has increased to 120 parts. The tempera-ture, however, may be varied between 180° and 260°, and the composition of the product varies with the temperature employed and the amount of chlorine absorbed. The product consists mainly of β-tetrachloranthracene (m.p. 152°), which is readily soluble in benzene and crystallises out in yellow needles, and another part much less soluble in benzene and more highly chlorinated. This latter consists of two products : hexachlor-anthracene (m.p. 277°), which crystallises from nitrobenzene, and heptachloranthracene (m.p. 232°), which is more soluble in benzene than the former. Oxidation converts these com-pounds into chloranthraquinones, containing 2 atoms of chlorine less than the original com-pound. Treatment with a mixture of nitric and sulphuric acids results in the formation of chlornitroanthraquinones which yield dyestuffs on treatment with fuming sulphuric acid. The chloranthraquinones on treatment with fuming sulphuric acid in the presence or absence of boric acid, yield hydroxy- compounds; e.g. 1 : 4 dichloranthraquinone yields *quinizarin* (q.v.) (Farb. vorm. F. Baeyer & Co., Fr. Pat. 385358 ; J. Soc. Chem. Ind. 1908, 557). Reducing agents, such as sodium amalgam or phosphorus and hydrogen iodide, convert anthracene into the dihydride (Graebe and Liebermann, l.c. ; Lieber-mann and Topf., Annalen, 212, 5) ; hydrogen and nickel oxide at 260°–270° and 100–125 atmos. convert anthracene first into tetrahydro-, then decahydro-, and finally perhydroanthracene (Ipatieff, Jokowleff, and Rakitin, Ber. 1908,

Estimation.—Luck (Ber. 6, 1347); Meister, Lucius, and Bruning (Dingl. poly. J. 224, 559); Nicol (Chem. Soc. Trans. 1876, 2, 553) ; Bassett

(Chem. News, 73, 178 ; 79, 157). The per-centage of anthracene in a sample of the commercial product is determined by oxidising it to anthraquinone with chromic acid, dissolving the product in sulphuric acid, and precipitating with water, since the associated impurities are either destroyed during the oxidation or are converted into sulphonic acids soluble in water. The details of the process are as follows : 1 gram of anthracene is introduced with 45 c.c. of acetic acid into a flask connected with a reversed condenser, and heated to boiling ; a solution of 15 grams of chromic acid in 10 c.c. of acetic acid and 10 c.c. of water is then added, drop by drop, to the boiling solution during a period of 2 hours ; and the product is boiled for 2 hours longer, allowed to stand for 12 hours, then poured into 400 c.c. of water, and, after standing for 3 hours longer, is filtered. The anthraquinone on the filter is washed with water, with hot dilute alkali, and then with hot water ; afterwards it is placed in a small dish dried at 100°, and digested for 10 minutes with 10 times its weight of pure concentrated sulphuric acid at 100°. The solution of anthraquinone is sulphuric acid is then allowed to remain for 19 hours in a moist atmosphere, mixed with 200 c.c. of water, and the precipitated anthraquinone filtered off and washed first with water, then with dilute alkali, and finally with water ; it is then dried at 100° in a dish, weighed, ignited, and the ash deducted from the first weighing. The difference gives the weight of anthraquinone corresponding to the amount of anthracene present in the sample.

Impurities.—Paraffin is usually present in crude anthracene, and is estimated by treating the material with fuming nitric acid, keeping the mass cold. When all the acid has been added, the mixture is kept at the ordinary temperature until the anthracene has dissolved, and then heated until the paraffin has melted. The solution is filtered and the precipitate washed with fuming nitric acid until the filtrate dissolves in water without turbidity, and then with water until neutral. Finally, the paraffin is washed with alcohol, dissolved in warm ether and the filtrates collected in a weighed porcelain dish ; the filtrates are evaporated and the paraffin dried at 105°–110° for half an hour (Heusler and Herde, J. Soc. Chem. Ind. 1895, 828). The detection of carbazole and phenanthrene in the purified product is carried out as follows :—

Carbazole. Sample is extracted in cold with ethyl acetate, solution allowed to evaporate, and residue transferred by a few drops of same solvent to a watch-glass. On evaporation, carbazole is left behind ; when treated with a drop of nitrobenzene and phenanthraquinone, it yields characteristic small copper coloured .

Phenanthrene. Sample is extracted with benzene, and the evaporation residue treated with α-dinitrophenanthraquinone in nitrobenzene. In this case mixed crystals are obtained having the form and colour of the brown needles of the phenanthrene compound, but containing a large quantity of anthracene.

ANTHRACENE ACID BROWN, -CHROME BLACK, -RED, -YELLOW *v.* Azo- COLOURING MATTERS.

ANTHRACENE GREEN. *Cærulein* and *Cærulein S.* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS; also XANTHINE COLOURING MATTERS).

ANTHRACENE VIOLET. *Gallein* (*v.* ALIZARIN AND ALLIED COLOURING MATTERS ; also XANTHINE COLOURING MATTERS).

ANTHRACHRYSONE *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRACITE *v.* FUEL.

ANTHRACITE BLACK *v.* AZO- COLOURING MATTERS.

ANTHRACOXENE *v.* RESINS.

ANTHRACYL CHROME GREEN *v.* AZO-COLOURING MATTERS.

ANTHRAFLAVIC ACID *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAGALLOL *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRAGALLOL DIMETHYL ETHERS *v.* CHAY ROOT.

ANTHRANIL, ANTHRANILIC ACID (*o-aminobenzoic acid*) *v.* AMINOBENZOIC ACID AND HOMOLOGUES.

ANTHRANOL. *9-Hydroxyanthracene*

$$C_6H_4 \underset{CH}{\overset{C \cdot (OH)}{<}} C_6H_4$$
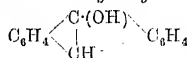
is prepared by the reduction of anthraquinone with hydriodic acid and phosphorus (Liebermann and Topf, Annalen, 212, 6 ; Ber. 1876, 1201), or with tin and acetic acid (Liebermann and Gimbel, Ber. 1887, 1854). Another method is to add copper or aluminium powder to anthraquinone dissolved in concentrated sulphuric acid at 30°–40°, and pour the product into water. The crude substance is recrystallised from glacial acetic acid containing a trace of aluminium and a little hydrochloric acid (Baeyer & Co., D. R. P. 201542 ; Chem. Zentr. 1908, ii. 1218 ; Bezdzik and Friedlander, Monatsh. 30, 871). Anthranol has been synthesised by heating 1 part of o-benzylbenzoic acid with 2 parts of sulphuric acid at 100° (Fischer and Schmidt, Ber. 1894, 2789). It crystallises in colourless needles, m.p. 165°, with decomposition. It dissolves in alkalis, and then behaves as its tautomeride anthrol (*q.v.*) ; *e.g.* it condenses with benzaldehyde to form benzilidine anthrol (Haller and Padova, Compt. rend. 141, 857, *v.* also Bad. Anil. und Soda Fab., D. R. P. 172930 ; Chem. Zentr. 1906, ii. 834). By heating the alkaline solution of anthranol for some time, it becomes oxidised to anthraquinone ; hydroxylamino hydrochloride converts it into anthraquinonedioxime (Nietzki and Kehrmann, Ber. 1887, 613). Anthranol yields a benzoyl derivative (m.p. 164°) with benzoyl chloride in pyridine (Padova, Compt. rend. 143, 121 ; Ann. Chim. Phys. [8] 19, 353), and a diiodide with iodine in benzene solution (Liebermann, Glawe und Lindenbaum, Ber. 1904, 3337).

Dianthranol $C_{28}H_{18}O_2$ is formed, together with a little anthraquinone, when anthranol dissolved in benzene is exposed to sunlight for some weeks, or when the benzene solution is boiled for some hours. Colourless tabular crystals m.p. 250°) (Orndorff and Bliss, Amer. Chem. J. 1896, 453 ; Orndorff and Cameron, Amer. Chem. J. 1895, 658).

ANTHRAPURPURIN v. ALIZARIN AND ALLIED
COLOURING MATTERS.

ANTHRAQUINONE $C_6H_4\diagdown\!\!\!\!\begin{array}{c}CO\\CO\end{array}\!\!\!\!\diagup C_6H_4$.
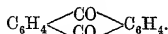
Obtained by the oxidation of anthracene with
chromic acid (Kopp, Jahresbericht. 1878, 1188 ;
Laurent, Ann. Chim. Phys. [2] 60, 220 ; 72, 415 ;
Annalen, 34, 287 ; Anderson, Annalen, 122,
301 : Graebe and Liebermann, Annalen, Spl. 7,
285) ; by the distillation of calcium benzoate
(Kekulé and Franchimont, Ber. 1872, 908) ;
by the distillation of benzoic acid with
phosphorus pentoxide ; by the distillation of
o-benzoylbenzoic acid with phosphorus pentoxide,
or by heating it alone (Ullmann, Annalen, 291,
24 ; Behr and Dorp, Ber. 1874, 578 ; Lieber-
mann, Ber. 1874, 805 ; Perkin, Chem. Soc.
Trans. 1891, 1012) ; by the dry distillation of
calcium phthalate (Panaotovits, Ber. 1884, 13).
Heller (Zeitsch. angew. Chem. 1906, 19, 669)
heats 1 part of phthalic anhydride with 3·5 parts
of benzene and 1·8 parts of aluminium chloride
in a lead vessel at 70° until the evolution of
hydrogen chloride ceases. After cooling, water
is added and the excess of benzene removed by
steam distillation. The solution is made
alkaline and boiled, and then on addition of
acid benzoyl benzoic acid is precipitated. On
heating this for one hour at 150°, anthraquinone
is obtained (cf. Piccard, Ber. 1874, 1785 ;
Friedel and Crafts, Ann. Chim. Phys. [6] 1, 523 ;
Müller, J. 1863, 393). Phenyl-o-tolylketone
gives anthraquinone on heating with lead oxide
or on oxidation with manganese dioxide and
sulphuric acid (Behr and Dorp, Ber. 1873, 754 ;
1874, 16 ; Thörner and Zincke, Ber. 1877, 1479).

Industrial preparation.—Crude anthracene
(55–60 p.c.) is slowly added to a hot solution
of potassium dichromate in a large wood vat
lined with lead. The solution is kept well
stirred and heated with steam until all the
anthracene has been added. The steam is
then cut off and sulphuric acid is run into the
mixture in the form of a fine spray ; the heat
generated by the reaction keeps the solution
boiling. The crude anthraquinone is then
separated by filtration and dried. It is dis-
solved in sulphuric acid without applying any
heat, and, when solution is complete, transferred
to a large vat lined with lead and boiled with
water. The precipitated anthraquinone is at
once separated by means of filter presses
from the soluble compounds ; the pressed cakes
are boiled with a solution of soda, and then
again filtered, pressed, dried, and finally sub-
limed (Levinstein, J. Soc. Chem. Ind. 1883,
219 ; Kopp. *l.c.*). Poirrier and Rosenstiehl
(Eng. Pat. 8431 ; J. Soc. Chem. Ind. 1887,
595) oxidise anthracene in a closed lead-lined
vessel by means of ferric sulphate. The vessel
is heated to 120°–150° during 72 hours, com-
pressed air being injected into the vessel. By
this means the anthracene is virtually oxidised
by the air, the ferric sulphate acting as a carrier
for oxygen. Another process consists in the
absorption of nitric oxides diluted with air, by
zinc oxide, copper oxide, or a similar oxide
of low basicity. Anthracene is mixed with
this, and a stream of air or oxygen is passed
through the mixture at 250°–350°, anthraquinone
being produced (Ch. Fabr. Grünau, Landshoff
& Meyer, D. R. P. 207170, 215335 ; J. Soc.
VOL. I.—T.

Chem. Ind. 1909, 360, 1310). Darmstädter
(Chem. Zentr. 1900, ii. 151 ; D. R. P. 109012)
prepares anthraquinone by the electrolytic
oxidation of anthracene in a chromic-acid bath.
Various processes have been patented for
purifying the crude anthraquinone thus pro-
duced. Bronner (J. Soc. Chem. Ind. 1882,
499 ; 1883, 410 ; Eng. Pat. 759 ; D. R. P. 21681)
dissolves out the impurities in a specially con-
structed circular shell. The method depends
on the continuous extraction of the impure
product with an amount of solvent insufficient
to keep in solution the whole of the anthra-
quinone and the easily soluble impurities.
Bayer & Co. (D. R. P. 68474 ; Eng. Pat. 5539 ;
J. Soc. Chem. Ind. 1893, 439) dissolve out the
impurities with liquid sulphur dioxide ; Sadler &
Co. Ltd. and Driedger (Eng. Pat. 17635 ; J. Soc.
Chem. Ind. 1902, 1072) recrystallise the crude
anthraquinone from hot aniline.

Properties.—Anthraquinone, as usually pre-
pared, forms a felted mass of crystals of a pale-
yellow or buff colour ; by sublimation it can be
obtained in the form of lemon-yellow needles or
golden-yellow prisms ; m.p. 277° ; b.p. 379°–
381° (corr.) (Recklinghausen, Ber. 1893, 1515) ;
sp.gr. 1·438–1·419 (Schroeder, *ibid.* 1880, 1071).
Sparingly soluble in alcohol and ether, some-
what more soluble in hot benzene. It is
neutral in its reactions, and is insoluble in
dilute acids or alkalis. Anthraquinone is
very stable ; it is not affected by hot hydro-
chloric acid, or by boiling with caustic potash or
calcium hydroxide solutions ; it dissolves in hot
nitric acid (sp.gr. 1·4), and is deposited in crystals
on cooling or on dilution ; it dissolves unchanged
in concentrated sulphuric acid at 100°, and is
precipitated in fine crystals on pouring into
water. Strongly heated with sulphuric acid,
it is converted into mono- and di-sulphonic acids
(*v.* ALIZARIN). Anthraquinone is of great com-
mercial importance, as it is used in the prepara-
tion of alizarin, quinizarin, purpurin, &c. (*v.*
ALIZARIN). Fusion with zinc or treatment with
sodium methoxide converts it into anthracene
(Haller and Minguin, Compt. rend. 120, 1105) ;
fusion with caustic soda converts it into sodium
benzoate (Graebe and Liebermann, Annalen,
160, 129), and by distilling it over lime benzene
is formed ; reduction with zinc and caustic
soda, or with sodium amalgam yields oxanthranol
$C_{14}H_{10}O_2$ and dianthranol (Diels and Rhodius,
Ber. 1909, 1076 ; Meyer, Ber. 1909, 143) ; zinc
and amyl alcohol converts it into dianthrol
(Meyer, Monatsh. 30, 165). Phosphorus penta-
chloride and phosphorus oxychloride convert
it into trichloranthracene and other chlorinated
products (Radulescu, Chem. Zentr. 1908, ii.
1032). A delicate test for anthraquinone
consists in reducing it with sodium amalgam in
dry ether. On adding a drop of water, a red
colouration is produced ; if alcohol is used
instead of ether, addition of water gives a green
colouration (Claus, Ber. 1877, 927).

Condensation products.—With phenols :
Scharwin and Kusnezof, Ber. 1903, 2020 ; 1904,
3616 ; Deichler, D. R. P. 109344 ; Chem. Zentr.
1900, ii. 360. With amines : Bayer & Co.
D. R. P. 86150, 107730, 136777, 136788, 148079 ;
Chem. Zentr. 1902, ii. 1272 ; Chem. Soc. Abst.
1904, i. 326. Aryl ethers, aryl- and alkyl-
amino- derivatives : Bayer & Co. D. R. P.

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158531; Fr. Pat. 354717, 362140; J. Soc. Chem. Ind. 1905, 885, 1105; 1906, 752. Thiocyanates : Bayer & Co. D. R. P. 206054; J. Soc. Chem. Ind. 1909, 239. Mercaptans : *ibid.* 469.

1.2- and 1.4-anthraquinones have been prepared from α-anthrol and 1.2 -anthraquinone from β-anthrol (*v.* Dienel, Ber. 1906, 926; Liebermann, Ber. 1906, 2089; Harlinger, Ber. 1906, 3537; Lagodzinski, Ber. 1894, 1483; 1895, 1422; 1906, 1717).

ANTHRAQUINONE RED *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHRARUFIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ANTHROL

$$C_6H_4 \left\langle \begin{array}{c} CH \\ | \\ CH \end{array} \right\rangle C_6H_3(OH).$$
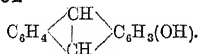
Two isomeric anthrols are known, α- or 1-hydroxyanthracene and β- or 2-hydroxyanthracene.

α-Anthrol is prepared by fusing 1-anthracenesulphonic acid with 5 parts of caustic potash at 250°, dissolving the mass in water, and filtering off the yellow flocks which separate out. The crude product is recrystallised from acetic acid and water. It forms yellow plates, m.p. 152°. α-Anthrol dissolves in the ordinary solvents with a blue fluorescence, and is more soluble than β-anthrol (Schmidt, Ber. 1904, 66; Dienel, Ber. 1905, 2862; *v.* also Linke, J. pr. Chem. [2] 11, 227).

β-Anthrol is prepared by fusing 2-anthracenesulphonic acid with potash and recrystallising the crude product from acetone (Liebermann and Hörmann, Ber. 1879, 589; Linke, J. pr. Chem. [2] 11, 222). It can also be obtained by reducing hydroxyanthraquinone with hydriodic acid and phosphorus (Liebermann and Simon, Ber. 1881, 123). It forms yellow plates melting with decomposition at 200°, and is soluble in the common organic solvents with a violet fluorescence. By reduction with sodium in alcoholic solution, dihydroanthrol is obtained (Bamberger and Hoffmann, Ber. 1893, 3069), and by heating with acetamide at 280° *anthramin* is obtained. Azo- dyestuffs have been obtained from β-anthrol (Act. Ges. f. Anilinf. D. R. P. 21178; Frdl. i. 538).

ANTIAR RESIN or **UPAS ANTIAR.** A green resin which exudes from the upas tree (*Antiaris toxicaria* (Lesch.), order Maraceæ). Light petroleum and benzene extract from it a substance analogous to caoutchouc, a fatty matter, and two resinous substances; alcohol extracts from the residue a very poisonous glucoside, *antiarin* (De Vrij and Ludwig, J. pr. Chem. 103, 253).

ANTIARIN *v.* GLUCOSIDES.

ANTI-CHLOR. Linen and cotton fibres and paper pulp are apt to retain some free chlorine from the hypochlorite used in bleaching, and as this causes the material to rot slowly, the manufacturers use certain reagents known as ' anti-chlors ' to remove the last traces of chlorine. The first substances employed were the neutral and acid sulphites of soda (sodium sulphite and bisulphite); these were superseded in 1853 by sodium hyposulphite, which is now very largely employed. Calcium sulphide, made by boiling milk of lime with sulphur; stannous chloride in hydrochloric acid with subsequent treatment with sodium carbonate to neutralise any free acid; ammonia, and sodium nitrite have also been recommended.

ANTIDIABETINE. Trade name for a preparation said to be composed of saccharin and mannite.

ANTI-FEBRIN. A trade name for *acetanilide* or *phenylacetamide* $C_6H_5 \cdot NH \cdot CO \cdot CH_3$. Discovered by Gerhardt in 1853, and investigated as an antipyretic by Kussmaul in 1886 (*v.* ACETANILIDE).

ANTIFORMIN. Trade name for the alkaline liquid prepared by adding caustic soda to a solution of sodium hypochlorite. Used as a disinfectant, the active ingredient being the chlorine, of which 4 p.c. is liberated on treatment with hydrochloric acid. Solutions of sodium hypochlorite are prepared in Germany by the electrolysis of 5 p.c. salt solution. A current of 110 volts and 100 amperes furnishes nearly 6000 litres daily of a disinfecting or bleaching solution containing 1 p.c. of available chlorine.

According to H. Will (Zeitsch. Ges. Brauw. 1903, 865; J. Soc. Chem. Ind. 1904, 125), it is one of the best disinfectants for brewery work. It rapidly softens organic impurities and facilitates their removal by scouring, in addition to its oxidising action, and it also dissolves incrustation. Its germicidal power is high, and a 5 p.c. solution is sufficient for most purposes. It is used cold, and may be safely applied to varnished surfaces with a brush, provided care is taken to prevent prolonged contact.

ANTIFUNGIN. Trade name for magnesium borate, employed as a fungicide.

ANTIGERMIN. Trade name for a preparation of a copper salt of a weak organic acid, mixed with lime. It is used as a fungicide.

ANTIHYPO. A solution of potassium percarbonate, used for destroying sodium thiosulphate in photographic negatives and prints.

ANTIMONIN. Trade name for antimony calcium lactate, used as a tannin-fixing mordant.

ANTIMONITE. Native antimony sulphide (*v.* ANTIMONY).

ANTIMONY. (*Antimoine,* Fr.; *Antimon,* Ger.) *Stibium.* Sym. Sb. At. wt. 120·2.

Occurrence.—Antimony occurs native in small quantities, occasionally in rhombohedral crystals, at Andreasberg in the Hartz, Przibram in Bohemia, Sala in Sweden, Allemont in France, in the United States, New South Wales, and Quebec. It occurs in large masses in Sarawak, Borneo.

Combined with *oxygen* as the sesquioxide Sb_2O_3, it occurs in *antimony bloom, white antimony,* or *valentinite,* and in *senarmontite,* being found in workable quantities in the Algerian province of Constantine. In *antimony ochre* or *cervantite,* and in *stibiconite* and *volgerite,* it occurs as antimonite of antimony Sb_2O_4.

Combined with *sulphur,* it occurs as *stibnite, antimonite,* or *grey antimony ore* Sb_2S_3. In union with *sulphur* and *oxygen* together, it forms *red antimony, antimony blende* or *kermesite* $Sb_2O_3 2Sb_2S_3$.

With *arsenic,* antimony is found in *allemontite* or *arsenical antimony.* With *silver,* in *discrasite.*

With sulphur and metals, antimony forms a number of *sulphantimonites,* among which may be mentioned *zinkenite, jamesonite, boulangerite,*

and *feather ore*, containing antimony, sulphur, and lead; *miargyrite*, *pyrargyrite*, and *stephanite*, containing silver; *berthierite*, containing iron, and *antimonial copper glance*. Antimony is found in certain ferruginous waters.

The antimony minerals of commercial importance as ores are *stibnite*, and the decomposition products which are usually associated with it and sometimes entirely replace it, viz. *kermesite*, *valentinite*, *senarmontite*, and *cervantite*.

Antimony ores occur in workable quantities in Mexico, California, North America, Canada, Australia, Japan, Borneo, Cape of Good Hope, New Zealand, Asia Minor, Algiers, Italy, Spain, Portugal, Corsica, and Sardinia. Small deposits of antimony sulphide have been discovered in Cornwall, Cumberland, and Scotland.

The veins in which stibnite is found are usually 4–6 inches in width, but in some rich mines, as in Nevada, they are several feet across. The gangue materials are quartz, with some brown-spar and heavy spar, and from these the sulphide can only be separated by handpicking or liquation. It is occasionally found in pockets, when it is usually very pure.

By far the most general ore of antimony is the sulphide, but in some cases, as in Algeria, the oxide is found in workable quantities, and in other cases both oxide and sulphide occur together.

Extraction.—Metallic antimony and its compounds are nearly always extracted from the ores by dry methods. According to their suitability for the several methods of treatment, the ores fall into two broad classes:

(*a*) Sulphide ores containing over 40 p.c. stibnite.

(*b*) Sulphide ores containing less than 40 p.c. of the sulphide, and oxide ores of any grade. In this class also may be included liquation residues and flue deposits, &c.

Preliminary treatment of ores.—Ores of class (*a*) are used for the production of the metal by the English process. If the content of sulphide is over 90 p.c., the ore requires no preliminary treatment, but less pure ore is subjected to a process of *liquation*, in which the sulphide is melted and allowed to run away from the gangue.

The following method of liquation was formerly used where fuel is plentiful, as at Malbosc, in the Department of Ardèche, Wolfsberg in the Hartz, and in Hungary. The ore was placed in small lumps in a number of conical pots of 45 kilos. capacity, each perforated below and standing on a perforated plate over a sunken receiver. The pots were surrounded by fuel which continued to burn for 10 hours, the melted sulphide collecting in the receivers.

At La Lincouln, Wolfsberg, and Haute Loire, the pots were contained in a reverberatory furnace. At Schmöllnitz, in Hungary, the melted sulphide ran through channels into receivers outside the furnace.

At Malbosc, the pots are replaced by cylindrical tubes, perforated below and standing on similarly perforated plates above the receivers. Each cylinder has a capacity of 500 lbs. of ore, four being heated in one furnace. Each has a hole at the side, through which the residues are removed, these holes being closed during the heating. The receivers are of clay, or of iron coated with clay.

The method of liquation in reverberatory furnaces is used in some places where ore can be mined cheaply but fuel is dear. The consumption of fuel per unit of sulphide liquated is east with this type of furnace, but there is a considerable loss of antimony by volatilisation. This loss, however, can be prevented by the use of suitable condensing apparatus such as Herrenschmidt's (*v.i.*).

In any process of liquation the temperature must be carefully regulated, as too low a temperature results in a low yield of sulphide, the residues containing too much antimony, while too high a temperature increases the loss by volatilisation.

Ores of class (*b*) are either roasted to the non-volatile tetroxide, or to the volatile trioxide, or are subjected to one of the direct reduction processes.

The oxidation of the sulphide to tetroxide takes place at temperatures between 350° and 400° in presence of excess of air. If the ore is impure, antimonates of the metallic impurities are formed at the same time. During the roasting there is a great tendency for the ore to frit, and this necessitates the constant rabbling of the charge. The presence of gangue renders the ore less liable to fuse, so that the process is most easily carried out with poor ores, *e.g.* ore-dust, for the treatment of which it is largely used. The furnaces employed are of two classes:

(*a*) Rabble furnaces, having an egg-shaped flat bed, with a furnace on either side and a working door at the front. With these the process is intermittent.

(*b*) "Fortschaufelungsofen," in which the roasting is carried on continuously. These furnaces are 40–45 feet long, by 8 feet high, by 2 feet wide, and have 10 working doors on each side. The ore is charged in at one end, and is then gradually worked along the bed during about 40 hours, and finally discharged at the other end. Fresh ore is continually charged into the furnace at the rate of 6 cwts. every 8 hours.

The oxidation of the sulphide to volatile trioxide takes place at about 400° with a carefully regulated amount of air. This process, provided suitable condensation apparatus is installed, presents marked advantages, and is finding an increasing application, especially in dealing with poor ores. It may be noted that arsenic is completely separated as the more volatile trioxide, that any gold or silver present is left in the residues and can afterwards be extracted, that there is no loss of antimony, and that the consumption of fuel is low. Many different forms of plant have been used for this process, but in most the roasting takes place in a cupola or reverberatory furnace. The earlier forms of condensing apparatus are of two classes:

(*a*) In which the vapours are passed through a series of flues and chambers and finally through water-tanks in which the last traces of oxide are deposited.

(*b*) In which the furnace gases are cooled below 100° in flues and then filtered through canvas or other coarse fabric (*v.* Chatillon, Fr. Pat. 189974, 1888; and 382504, 1907; Woolford, Fr. Pat. 200245, 1889; Plews, U.S. Pat. 704367, 1902). Herrenschmidt has patented a complete plant for this process (Fr. Pat. 333306,

1903, and 386107, 1908), which differs materially from any earlier apparatus.

The roasting furnace is partly of brick and partly cast metal, and is provided with a hopper through which the ore, mixed with 4–5 p.c. of gas-coke or 6–7 p.c. charcoal, is introduced. The gases pass from the furnace into a chamber, and then through a series of cast-iron tubes placed nearly vertical and air-cooled, in which the main portion of the trioxide is deposited. The last traces are removed by forcing the gases up a tower filled with coke over which water flows. The draught is maintained by two centrifugal fans, working tandem. It is stated that 6 tons of ore, containing 10–15 p.c. antimony, can be treated in 24 hours, with a yield of over 90 p.c., and that the cost of producing 1 ton of oxide is 70 francs.

Smelting of the metal.—Antimony is prepared from ' crude antimony ' or high-grade stibnite ores by the ' English ' or ' precipitation ' method. The ore, of which the composition has been determined by analysis, is ground under edge-runners to the size of a hazel-nut, or smaller, and is subjected to three operations :

Singling. This process is carried out in crucibles of which about forty are arranged in a double row on the hearth of a long reverberatory furnace having a grate at each end, and a flue, leading to condensing chambers, in the middle. The crucibles are about 20 inches high and 11 inches across, and are made of a mixture of 6 parts fire-clay and 1 part plumbago. The charge for each pot is 42 lbs. ore, 16 lbs. iron (of which about 2 lbs. is in the form of turnings, and 14 lbs. as tin-plate cuttings beaten into a ball), 4 lbs. salt, and 1 lb. slag from ' doubling ' (*v.i.*). These materials are introduced into the red-hot crucible, and kept in a state of fusion for 2–3 hours, at the end of which time the contents are poured into moulds, and the antimony is removed from beneath the slag. The product, known as *singles*, usually contains about 91 p.c. antimony.

Doubling is carried out in crucibles arranged in a furnace as previously described. The charge for each pot is 84 lbs. broken singles, 7–8 lbs. liquated sulphide, and 4 lbs. salt, and the fusion, which takes about 1½ hours, is closely watched, the workmen judging from the nature of the slag when the operation is complete. The slag is then removed with an iron ladle, and the metal run into moulds. This product is called *bowl metal* or *star bowls*.

Frenching, or *melting for star metal* (*v.i.* under

In the English process the loss due to slagging and volatilisation is small, being only 2–5 p.c.

The sulphide may be mixed with half its weight of charcoal to prevent caking, and roasted at a gentle heat, the heat being gradually increased, but not to melting, whereby large quantities of sulphurous acid, arsenious oxide and antimonious oxide are evolved, the two latter being collected in flues. 20 p.c. of the antimony is stated to pass off in this operation, the greyish or red mass which remains consisting of antimony tetroxide containing about one-sixth of its weight of the trioxide and some sulphide. This residue, known as antimony ash, is mixed with 0·5 part of cream of tartar, or 1 part

charcoal and 0·5 part of potash, or ⅓ part charcoal saturated with a concentrated solution of sodium carbonate, and fused in a covered crucible at a low red heat, and poured into a hot mould. 100 parts of sulphide yield 44 parts of antimony. The slag which rises above the metal consists of alkaline carbonate mixed with double sulphide of antimony and potassium or sodium with charcoal, and is known as *crocus of antimony*. The action of the charcoal in this reduction consists in the removal of the oxygen from the antimony oxide, producing metallic antimony, and in the reduction of a part of the alkali. The alkaline metal thus set free combines with the sulphur of a part of the antimonious sulphide, freeing an equivalent quantity of the antimony and forming a double sulphide of antimony and potassium with a further quantity of the sulphide.

The sulphide may also be reduced by fusing 8 parts of sulphide with 6 parts of cream of tartar in a crucible heated nearly to redness, then adding 2 or 3 parts of potassium nitrate, and fusing until perfectly liquid ; or 8 parts of sulphide are mixed with 6 parts of cream of tartar and 3 parts of nitre, and are thrown in portions into a red-hot crucible and heated until perfectly fluid. By quietly fusing, with frequent stirring to prevent frothing, a mixture of 8 parts sulphide, 1 part sodium carbonate, and 1 part charcoal, 66 p.c. of metal is said to be obtained from the sulphide.

It is possible also to reduce the sulphide on the hearth of a reverberatory furnace. The partially roasted ore, which contains the sulphide and oxides of antimony, is mixed and fused with 8–13 p.c. of coal and 9–11 p.c. of soda, frequently with the addition of iron, in which case the slag produced is much less fusible and does not entirely cover the bath of metal ; the antimony produced also contains much iron (Dingl. poly. J. 162, 449). Where carbonate of soda is used for the fusion the mass froths considerably and attacks the furnace hearth.

The metal is prepared from either of the oxides by one of the numerous reduction processes now in use.

(*a*) Reduction in reverberatory furnaces is carried out at Bouc, Septèmes, New Brunswick, &c. The furnace-bed is egg-shaped, deep in proportion to its width, and is provided with a tap-hole at the lowest point. The furnace gases are passed through a long series of condensing chambers. First 90–110 lbs. flux (chiefly salt, with some soda and sodium sulphate) and 220–230 lbs. of slag from a previous operation are melted on the hearth, and then 400–500 lbs. of roasted ore and 67–75 lbs. of charcoal are added, and the whole kept in a state of fusion till reduction is complete. At New Brunswick the reduction and refining are carried out consecutively in the same operation.

(*b*) Some French smelters reduce an oxidised ore containing 30–40 p.c. of antimony in a 3-tuyered shaft furnace at the rate of 2–2½ tons per 24 hours, with the consumption of about half that weight of coke. The regulus contains 92–95 p.c. of antimony, and is subsequently refined.

At Bánya, Hungary, antimony ores are mixed with silicious material and smelted in a blast-furnace for impure regulus, which is then

refined in a reverberatory furnace. The blast-furnace used is a round stack 6 m. high and 1·4 m. diameter at the throat. The hearth, which is 1 m. across, is fitted with five water-jacketed tuyeres, and has two outlets for slag and metal respectively; a third opening is used for blowing out. A blast of 15 c.m. per minute is used, and the gases are collected by a tube at the throat and passed through a condensing apparatus. Such a furnace will run for 3 weeks continuously, smelting about 20 tons of material daily. Berg. u. Hütt. Zeit. 1886, p. 102).

(c) Reduction in crucibles is only used when rich ore or the trioxide is available. The reducing agent is carbon (charcoal or anthracite), and sodium sulphide and carbonate are added to .

Considerable quantities of antimony ore are now treated directly for the production of the metal. One such process which has been success-fully used for some time depends on the reduction of the sulphide in a bath of molten ferrous sul-phide containing iron (v. T. C. Sanderson, U.S. Pat. 711010, 1902; Cookson, Fr. Pat. 324864 1902; and Herrenschmidt, Fr. Pat. 296200, 1900).

Another method consists in the reduction of the sulphide with carbon in water-jacketed blast-furnaces. This has been used by Hering for the treatment of liquation residues.

Germot (Revue des Produits Chemiques, Dec. 15, 1907) and Herrenschmidt (Fr. Pat. 333340, 1903) have used converters for the smelting of sulphide ores.

Methods of treating antimony ores have also been proposed by which the antimony is con-verted into the volatile chloride, as in Lyte's process of roasting the ore with salt. The ore may also be subjected to the action of hydro-chloric acid gas in a reverberatory or muffle furnace, the volatilised chloride being condensed in a solution of hydrochloric acid (Dingl. poly. J. 250, 79–88, and 123–133).

Among processes allied to the smelting of antimony there need only be mentioned that of Herrenschmidt for the extraction of gold from antimony (Fr. Pat. 350013, 1904). This de-pends on the fact that when a small quantity of antimony is melted with or reduced from auriferous stibnite, all the gold present in the sulphide passes into the metal.

Many proposals have been made for the ex-traction of antimony by wet or electrolytic methods, but they have not been a success commercially. Reference may be made to Hering (Dingl. poly. J. 230, 253), and Borchers (Electrolytische Gewinnung des Ant. Chem. Zeit. xi. 1883, 1023).

Refining of Antimony.

Unrefined antimony contains sulphur, iron, arsenic, and sometimes copper and lead. The following analyses show the composition of typical samples, I. and II. being metal made with scrap iron, the arsenic and gold being due to admixed pyrites; III. and IV. metal from roasted ore smelted in a blast furnace:—

	I.	II.	III.	IV.
Antimony	94·5	84·0	97·2	95·0
Iron	3·0	10·0	2·5	4·0
Sulphur	2·0	5·0	0·2	0·75
Arsenic	0·25	1·0	0·1	0·25
Gold	traces	—	—	—

All these impurities, except lead, can be removed by slagging with oxidising, sulphurising, or chlorinating agents. The usual fluxes are: Glauber salt and charcoal, which remove copper and iron as sulphides, and arsenic as sodium arsenate; and antimony glass (antimony oxysulphide) which eliminates sulphur. Chlor-ides, such as salt or carnallite, must be used with caution, or great loss by volatilisation may result.

Refining in crucibles finds its chief application in the English process. The 'star bowls' (v.s.) are cleaned from slag by chipping with sharp hammers, and the metal is then broken small and melted with 2–3 p.c. of antimony flux, pre-pared by melting together American potashes and powdered stibnite in varying proportions (approximately 3 parts potashes and 2 parts stibnite) until, by experiment, the correct com-position is found. The refining is carried out in the pots nearest the grates, and takes 30 minutes to 1 hour, the charge for each crucible being 84 lbs. The finished product is run into 8-lb. ingots, which are carefully surrounded with slag and allowed to cool without disturbance. The coal consumption is large, but is com-pensated by a much smaller loss by volatilisation than occurs in other processes.

Refining in reverberatory furnaces is used at Milleschau, Bánya, Siena, and Oakland. It is imperative that the bed of the furnace should be tight and able to withstand the action of the alkali flux, and this is best attained by making it of one solid piece of soft, weathered granite. A fairly good substitute for the granite is a mixture of burnt and raw clay well rammed into an iron box. An example of such a process is that recommended by Helmhacker and used at Milleschau (Berg. u. Hütt. Zeit. 1883, 191; and Dingl. poly. J. 250, 123).

A 'glass of antimony' is prepared by fusing a mixture of the crystalline antimony oxide which collects on the hotter portions of the flues with sulphide of antimony, until it forms a glassy dark grey or brown mass; this is mixed with the carbonate for the purification of the metal, and is occasionally used alone where the metal is but slightly impure

The bed of the furnace is heated to a cherry red and 600 to 700 kilos. of crude antimony placed on it; a quantity of oxide and some arsenic escape, and in from 30 to 60 minutes the metal has run down. From 3 to 7 p.c. (according to the purity of the metal) of carbonate of soda, sometimes mixed with coal or coke, is then added. The metal is thus covered and fumes less, small jets of flame appearing occasionally on its sur-face; the temperature is raised, the metal remaining under the slag for from 1 to 3 hours (determined by the workman), the slag then becomes thick, and is removed by drawing it through the door with a long-handled flat transverse iron.

Three p.c. of antimony sulphide and 1½ p.c. of oxide are then thrown on the surface of the metal, and when melted 4½ p.c. carbonate of potash, or of a mixture of carbonate of potash and soda, are added. By this means the iron and last traces of sulphur are removed; in less than 15 minutes the refining is complete, and the critical operation of ladling is performed. A cast-iron hemispherical ladle, holding 15–20

kilos., is riveted to a chain hanging from the roof exactly in front of the working door, before which the cast-iron moulds for receiving the metal are arranged on a stone table. The workman dips his ladle obliquely, removing some slag with the metal; part of this is first poured into the mould to prevent the metal from actually touching the mould, and the metal is well covered with the slag and left at rest. Unless this be done the 'starring' will be imperfect, and, as this is considered a test of purity, its value will be lowered in the market. The slag may generally be used again. The oxide condensing in the flues is removed as seldom as possible, as this operation, as well as the furnace work, is very injurious to the workers.

The cost of refining 100 kilos. of regulus is from 4 to 5 shillings.

Star antimony usually contains small amounts of iron, lead, sulphur, and arsenic, but can be further purified by Liebig's method, which consists in fusing the metal successively with 12 p.c. sodium carbonate and 6 p.c. antimony sulphide, and again with sodium carbonate to which a little nitre has been added.

Unlike many other metals, antimony carries on its face its own character for purity. When 'pure,' a beautiful fern leaf or 'star' appears upon its surface, and according to the length and form of this 'star' on the ingot its quality is determined. The presence of a relatively small percentage of impurities in the metal will prevent it from 'starring.' It is this peculiar characteristic of pure antimony to crystallise on the ingot in the fern-leaf or star form when cooling, which originates the trade term of 'star antimony' for good quality of antimony.

For pharmaceutical purposes it is important to prepare antimony quite free from arsenic. This may be accomplished by Wöhler's method. A mixture of 4 parts powdered commercial antimony, 5 parts sodium nitrate, and 2 parts sodium carbonate (to prevent the formation of insoluble antimony arsenate) is thrown into a red-hot crucible. Combustion takes place quietly, the mass is pressed together and more strongly heated for half an hour, so as to become pasty without fusion, being pressed down as it rises from evolution of gas. While still hot and soft, it is removed, reduced to powder, and boiled with frequent stirring in water, the finer powder is poured off with the water, and the residue again treated, the washings being mixed with that first obtained. The water, which contains the whole of the arsenic but no antimony (Meyer), is removed from the insoluble portion by subsidence, decantation, and filtration. The residue of sodium antimonate should be white, but the presence of lead imparts a yellow colour. It is dried and fused with half its weight of cream of tartar at a moderate heat, cooled, broken into small lumps, and the potassium and sodium removed by digestion in water. The powdered metal is then fused into a button.

This method may be used quantitatively for the separation of antimony from arsenic. If the sodium nitrate be replaced by potassium nitrate, a portion of the antimony will enter into solution with the arsenic as potassium antimonate (v. C. Meyer, Annalen, 46, 236; Chem. Zentr. 1348, 828). Arsenic may also be completely removed by fusing the antimony in succession

with 1st, potassium carbonate; 2nd, potassium nitrate; 3rd, antimonic oxide; 4th, potassium carbonate (Th. Martins, Kastn. Arch. 24, 253), or by fusing three times with fresh portions of sodium or potassium nitrate.

Duflos (Kastn. Arch. 19, 56) recommends a process in which the arsenic is driven off as fluoride by means of sulphuric acid and fluorspar. (See further Schw. 42, 501; also Buchner and Herberger, Repert. 38, 381, 256.)

Pure antimony may be obtained by heating tartar emetic to low redness and digesting the resultant mass in water to remove the potassium. The powder thus obtained may then be dried and fused into a button.

Tests for Impurities in Antimony.

Sulphur. The powdered metal evolves sulphuretted hydrogen gas (which blackens lead paper) on heating with strong hydrochloric acid.

Potassium or sodium. The metal is greyish and loses its lustre on exposure to air; it has an alkaline taste and reaction, and evolves hydrogen on immersion in water.

Arsenic. If deflagrated with ½ its weight of sodium nitrate, boiled with water and filtered, the arsenic enters into solution, leaving the antimony behind; the solution is saturated with sulphuretted hydrogen (if an orange precipitate, consisting of antimony sulphide, falls, this must be filtered quickly; it is due to the presence of a trace of antimony in the solution). The arsenic is deposited as the lemon-yellow sulphide on standing.

Lead and copper. The metal is powdered and treated with dilute nitric acid, evaporated nearly to dryness, taken up with water and filtered; the addition of sulphuric acid precipitates white lead sulphate, and the addition to the filtrate of potassium ferrocyanide gives a brown precipitate in presence of copper.

If sulphur as well as lead be present in the antimony, the lead is converted at once into sulphate by the action of nitric acid, the residue on evaporation is digested with yellow ammonium sulphide, which dissolves the antimonic oxide and leaves black lead sulphide.

Iron. The powdered metal is ignited with three parts nitre and washed with boiling water, the residue is boiled with hot dilute hydrochloric acid; on the addition of potassium ferrocyanide a blue precipitate is produced.

When antimony containing arsenic and iron is heated on charcoal, it gives a garlic odour and becomes coated with oxide of iron; it ceases to burn on removal of the flame, and yields a dull surface and yellow oxide (Liebig). The pure metal under such circumstances burns brilliantly and becomes coated on cooling with white crystals of the oxide.

Detection of antimony. When fused on charcoal with potassium cyanide or sodium carbonate or a mixture of the two, antimonial compounds produce a brittle white bead of metallic antimony with white fumes and a white incrustation on the charcoal; the bead leaves a white residue on treatment with nitric acid, which is soluble in cream of tartar or tartaric acid. Sulphide of antimony melts readily in the candle flame.

A delicate confirmatory test, given by Crookes, is to add to the white incrustation on

the charcoal one drop of ammonium sulphide, when the formation of the orange sulphide is conclusive evidence of the presence of antimony.

Estimation of antimony.—Fire assay. In valuing ores containing the sulphide the ore is broken into pieces about $\frac{1}{3}$ to 1 inch diameter, and from 2000 to 7000 grains of the lumps (avoiding dust), according to the probable richness of the ore, are selected. A Hessian crucible with a hole at the bottom covered with a piece of charcoal, is placed within another crucible of such size that the upper one enters about 1 inch. The ore, mixed with charcoal of about equal quantity and size, is placed in the upper crucible, covered with a layer of charcoal and luted down. Heat is then applied, the lower crucible being below the furnace bars and surrounded by ashes to keep it cool. The heat should be maintained at a cherry red, but not higher, for from 1 to $1\frac{1}{2}$ hours. On cooling, the regulus is removed from the lower crucible and weighed. It should be well fused, bluish-grey, and of bright fibrous crystalline fracture, the residue in the upper crucible should be examined to see if it is free from visible sulphide. As the sulphide contains 71·8 p.c. of antimony, the percentage of available antimony in the ore may be roughly calculated.

The fire assay of an ore for metallic antimony is carried out as follows : If the ore contains sulphide, it is roasted to oxide at the lowest possible temperature in a scarifier. Oxide ores need no preliminary treatment. The charge is made up of ore, 10 grams ; sodium bicarb., 25 grams ; argol, 5 grams ; salt to cover ; and is heated carefully in a clay crucible for the shortest time and at the lowest temperature that will ensure complete reduction. The resulting metallic button is cleaned by washing, and weighed.

Wet assay.—(a) Gravimetric. The antimony is obtained in solution as antimonate or antimonite, and hydrogen sulphide is passed into the cold liquid for 20 minutes. Then, without stopping the current of gas, the solution is heated to boiling, and the gas allowed to pass for another 15 minutes. The resulting precipitate of sulphide may then be subjected to one of two methods of treatment. It may be collected on a Gooch crucible, washed with hot dilute acetic acid saturated with hydrogen sulphide and heated to constant weight at 230° in a current of carbon dioxide. Or the precipitate may be collected on a filter, washed successively with hot water, alcohol, equal parts alcohol and carbon disulphide, alcohol, and, finally, ether, and then dried. The greater part of the precipitate is transferred to a watch-glass, and that still adhering to the paper is dissolved in a little hot ammonium sulphide, and the solution allowed to run into a weighed porcelain crucible. This is then evaporated to dryness, the main portion of the precipitate added, and the whole treated with fuming nitric acid and warmed, the crucible being covered with a watch-glass. When the violent action has subsided, the contents of the crucible are evaporated to dryness, again treated with nitric acid, and finally evaporated to dryness and heated to redness till the weight is constant. The antimony is then weighed as tetroxide.

(b) Volumetric. The most important volumetric method is that of Möhr, in which antimony trioxide or any antimonious compound is dissolved in a solution of tartaric acid, neutralised with sodium carbonate, treated with a cold saturated solution of sodium bicarbonate in the proportion of 10 c.c. to each 0·1 gram Sb_2O_3, and quickly titrated with $N/10$-iodine solution, using starch as indicator.

(c) Electrolytic. Classen and others have shown that if antimony sulphide (*v.s.*) is dissolved in the minimum amount of concentrated solution of sodium sulphide, and treated with excess of sodium sulphite, or, better, potassium cyanide solution (to destroy polysulphides), the liquid can be successfully electrolysed in the cold with a current of 0·25–0·5 amp., using a platinum dish as cathode. The process takes about 12 hours, and gives a good coherent deposit of metal which can be washed with water, alcohol, and ether, and finally dried and weighed.

Properties of Antimony.

Antimony is a lustrous, bluish-white metal, which has a coarsely laminated or granular structure, according as it has been slowly or quickly cooled. By partial solidification it can be obtained in obtuse rhombohedra, approximating to cubes.

The sp.gr. of the metal is 6·72–6·86. It melts at 630·5°C. (Heycock and Neville, Chem. Soc. Trans. 1895, 186), and boils at about 1350° in a current of hydrogen. Antimony has a hardness of 3–3·5, and is so brittle that it can readily be powdered. It is a bad conductor of heat and electricity.

The most important physical property of antimony is that of expanding on solidification, a property possessed also by its alloys. At the ordinary temperature it is not acted on by the air, but oxidises quickly on melting, and burns at a red heat, producing white fumes of the trioxide. It is oxidised by nitric acid of various strengths, dilute acid producing principally the trioxide, and the concentrated acid producing the pentoxide (H. Rose, Analyt. Chem. 1, 258). Dilute sulphuric and hydrochloric acids are without action on it, but the strong acids produce the sulphate and chloride respectively. When fused with borax or other vitrifying material, it imparts to them a yellow colour.

Antimony combines directly with the halogens with evolution of light and heat, and also, at a higher temperature, with the elements of the sulphur group, and with phosphorus and arsenic. The element occurs in three modifications : (1) the crystalline or ordinary form described above ; (2) an amorphous yellow modification, soluble in carbon disulphide, which is produced by the action of oxygen on liquid stibine at −90° ; and (3) the amorphous explosive antimony, which is best prepared by the action of a weak constant electric current on a concentrated acid solution of antimony trichloride, the strength of current bearing a constant relation to the surface of deposition, not less than $\frac{1}{2}$ grain being deposited per sq. inch per hour. Thus produced, it is bright and steellike in appearance, with an amorphous fracture, and sp.gr. 5·78. When heated to 200°, or struck or scratched, it rapidly changes into the crystalline form, increasing in density, with

the production of great heat. Antimony trichloride is always contained in the metal to the extent of 4·8–7·9 p.c., and is given off when the form changes. It is probable that this substance is a solid solution of an antimony halogen compound in an allotropic form of antimony, and that the explosion consists in the rapid transformation of the latter into the stable form. The change is accompanied by an evolution of heat amounting to 20 cals. per gram. Cohen and others (Zeit. physikal. Chem. 1904, 47, 1 ; 1905, 50, 291 ; 52, 129) have shown that this change goes on slowly when explosive antimony is preserved.

Antimony is precipitated as a fine powder by the action of zinc on an acid solution of an antimony salt. In this form it is sold as 'iron black' for producing an appearance of polished steel on papier maché, plaster of Paris, and zinc ornaments.

Brass can be covered with a fine lustrous coating of antimony by dipping in a hot mixture of 1 part tartar emetic, 1 part tartaric acid, 3 or 4 parts powdered antimony, 3 or 4 parts hydrochloric acid, and 3 parts water.

It may be deposited electrolytically on brass or copper by using a bath of the double chloride of antimony and ammonia acidulated with hydrochloric acid.

Alloys of Antimony.

Antimony alloys with most of the heavy metals and with the alkaline metals. It generally increases the fusibility, brittleness, and hardness of the metals with which it is combined, and imparts the valuable property of expanding on solidification, thus producing very fine impressions. The alloys of silver, gold, and lead with antimony have a greater density than the mean of the constituents, while those of iron, tin, and zinc are of less density. The sharpest impressions are produced when any of these alloys are cast at a low temperature (J . Soc. Chem. Ind. 1, 982). The castings are usually made in brass moulds coated with lampblack and turpentine.

With *lead*, antimony mixes readily in all proportions. By the addition of antimony to red-hot lead, alloys which crystallise in rhombohedra have been obtained by F. de Jussieu (Compt. rend. 38, 1321–1322). An alloy of equal parts of lead and antimony is very brittle, and rings when struck. Nasmyth has recommended the addition of 5 p.c. antimony to lead for use instead of bronze in taking casts of works of art (Athenæum, No. 1176, 511).

Type metal is essentially an alloy of lead and antimony, frequently with addition of tin and containing less frequently bismuth or copper. A few examples of common type-metals are :

	Lead	Antimony	Tin	Copper	Bismuth
Type metal	55	30	15		
,,	70	18	10	2	—
,,	50	28		—	22
Stereotype plate	85·7	14·3	—		
,, ,,	70	15	—	—	15
Linotype metal	84·5	13·5	2		

Wetterstedt's patent ship sheathing consists of 100 lead to about 3 antimony, but does not appear to have been used to any extent. The alloy, containing varying proportions of antimony, is also used, under the name of hard lead, in lead pipes, for making pumps and taps for raising acid in alkali works, in the manufacture of cannon-balls and shot, and for the emery wheels and tools of the lapidary.

Tin forms numerous useful alloys with antimony, especially with the addition of other metals. *Common Britannia metal* consists of tin 140, copper 3, antimony 9. Britannia metal for castings : tin 210, copper 4, antimony 12 ; ditto for lamps : tin 300, copper 4, antimony 15. The best Britannia metal contains tin 90, antimony 10, lead and bismuth being carefully excluded. Copper also is never added except for the production of colour. The exact proportion of antimony used depends on the quality of the tin, and is always ascertained experimentally. Increasing the proportion of antimony raises the m.p., increases the hardness, and decreases the malleability of the alloy. Good alloys take a brilliant polish, and show a fine-grained, jagged fracture. The presence of arsenic in the antimony diminishes the ductility of the product (*v.* BRITANNIA METAL). Superior pewter is made by fusing together tin 12, copper 1, antimony 1.

Metal argentum contains tin 85·5, antimony 14·5.

Ashbury metal : tin 77·8, zinc 2·8, antimony 19·4. Ships' nails, tin 3, lead 2, antimony 1.

Minofer is tin 68·5, antimony 18·2, copper 3·3, and zinc 10.

Bearing or *anti-friction metal* usually contains antimony, tin, and copper, but the composition is very variable, and some cheap varieties consist chiefly of iron or zinc. Occasionally lead and tin or lead and zinc are alloyed with antimony to form bearing metals. As the name indicates, it is used for machinery bearings, being especially suitable for light loads at high speeds. As examples of these alloys the following may be given :—

	Antimony	Tin	Copper	
Babbit's metal	8·3	83·3	8·3	—
Very hard bearings	5	2·5	Iron 70
Cheap bearings	1·7	7	Zinc 90
U.S. Rly. Babbit metal	7·4	88·9	3·7	—
German Rly. Babbit metal	11·1	88·3	5·6	—

Copper. The presence of 0·15 p.c. of antimony renders copper both cold and hot short. With varying proportions of the two metals, shades from pure copper-red to rose-red, crimson, and violet may be obtained, the last when equality is reached. Two definite compounds of copper and antimony appear to exist, viz. $SbCu_2$, a violet alloy known as 'Regulus of Venus,' and $SbCu_4$ (Kamensky, Phil. Mag. [5] 17, 270 ; *v.* also Ball, Chem. Soc. Trans. 1888, 167).

Antimony is frequently added to brass to heighten its colour. These alloys are harder and finer in texture than copper or brass, and take a better polish. Antimony is sometimes added for this reason to the material for concave mirrors. It is also added occasionally to bell metal, as it is believed to add to the intensity and clearness of the sound. Many celebrated old bells contain antimony, *e.g.* 'Old Tom' of Lincoln, which contains about 0·03 p.c.

Zinc. Antimony forms definite crystalline compounds with zinc, which, however, differ widely in composition while retaining the same

form. They decompose water rapidly at the boiling temperature, and this action is promoted by the presence of traces of platinic chloride. Cooke has suggested the suitability of this reaction for the preparation of pure hydrogen.

Iron containing less than $\frac{1}{4}$ p.c. of antimony is both hot and cold short. A mixture of 7 parts antimony and 3 parts iron heated to whiteness with charcoal forms a hard white alloy which strikes sparks with steel.

Alloys of *antimony* and *aluminium* have been described by Pécheux (Compt. rend. 138, 1606), which vary in composition from $SbAl_{30}$ to $SbAl_{40}$, having a density of $2\cdot73-2\cdot60$, and m.p. $760°-730°$. These alloys expand on solidifying, and are hard, but fairly malleable. They are unaltered by air or water at ordinary temperatures, and this property, combined with their lightness and malleability, should render them useful in the building of light structures such as aeroplanes.

Melted gold absorbs the vapour of antimony, but gives it up almost entirely on further heating. Gold loses its malleability when $\frac{1}{2000}$ of antimony is present. An alloy of 9 gold and 1 antimony is white and very brittle, with an amorphous porcelain-like fracture. Silver antimonide occurs as the mineral *discrasite*.

COMPOUNDS OF ANTIMONY.

The principal compounds of antimony are formed by combination with oxygen, sulphur, and chlorine; some compounds contain two of these negative elements, of which the oxychloride or *powder of Algaroth*, and the oxysulphide or *glass of antimony* are examples.

The most important of these are the trichloride, trisulphide, and trioxide.

Antimony trisulphide Sb_2S_3.

Crude antimony, antimony ore, sesquisulphide of antimony; Schwefelspiessglanz; Grau-Spiessglanzerz; Stibium sulphuratum nigrum; lupus metallorum.

This substance, as it occurs naturally, or after liquation, is usually too impure to be employed for other purposes than the preparation of the metal.

The ordinary sulphide may be prepared by the following methods :—

(1) Thirteen parts pure antimony are mixed with 5 parts flowers of sulphur, and projected in portions into a red-hot crucible; when completely fused, it is poured out and any free metal detached.

(2) Sulphuretted hydrogen precipitates it as an orange precipitate from a solution of an antimony salt.

(3) Digest for two hours in a closed vessel 1 part crude antimony sulphide, 1 part pearl ash, $1\frac{1}{2}$ parts lime, and 15 parts water, and add sulphuric acid; the alkaline sulpho- salt first formed is decomposed by the acid with the precipitation of the pure sulphide. Antimony sulphide is soluble in alkaline sulphides and in acid potassium sulphate. When finely powdered and rubbed to a paste at $20°$ or $30°$ with strong sodium sulphide solution, a coppery metallic mass is produced, and the liquor, on addition of more sodium sulphide, yields Schlippe's salt.

The sulphide is used to some extent in refining gold from silver and copper, and in the preparation of safety matches and percussion

pellets for cartridges, in pyrotechny and in veterinary surgery.

Kermes mineral. *Brown-red antimony sulphide. Pulvis Carthusianorum. Sulph. stibiatum rubrum.*

Kermes mineral usually consists of a mixture of the trisulphide and trioxide containing alkali. Berzelius and Rose state that some samples examined by them consisted of a true double sulphide of potash and antimony.

Preparation.—Fuchs asserts that if antimony sulphide is heated and *suddenly* cooled in water it yields an orange-red, less dense powder of kermes. A. Ditte (Compt. rend. 102, 212) does not confirm this statement.

(1) Four parts pure potassium carbonate and 11 parts pure antimony sulphide are heated to fusion in a covered crucible, cooled, boiled with water, and filtered. The solution on exposure to the air deposits kermes, the residue from the first boiling is heated with the mother liquor from some previously deposited kermes, and yields a further quantity ; this operation is repeated until an insoluble residue of trisulphide and trioxide is left. Each successive deposit of the kermes contains a larger amount of the oxide.

(2) Fuse together 2 parts antimony, 1 sulphur, and 3 sodium carbonate; or, 1 antimony sulphide and 3 or 4 tartaric acid, until fumes cease to be evolved; and treat the product as in (1).

(3) The slags from the reduction of antimony ore with cream of tartar slowly precipitate kermes when treated with water ; this is sold to veterinary surgeons as ' kermes by the dry way.' When antimony sulphide is boiled with potash and precipitated with an acid, the kermes produced contains no oxide (Liebig). The kermes produced by the action of *dilute* alkaline carbonate on antimony sulphide also contains no oxide (Rose). The oxide may be removed from ordinary kermes by digestion with tartaric acid. A solution containing so much alkali as to give no precipitate on cooling gives, when treated with carbonic acid gas, a highly sulphurated kermes containing antimony pentasulphide.

Kermes is a brown-red, loosely coherent powder, with a brown streak, containing water, which is given off below $100°$. It is lighter than the ordinary sulphide. The kermes containing antimony oxide, when fused and solidified, is destitute of crystalline structure, while that free from oxide produces a highly crystalline solid.

Antimony pentasulphide Sb_2S_5. *Golden sulphide of antimony ; sulphur antimonii auratum.*

Prepared by boiling the trisulphide with potash and ground sulphur, filtering and precipitating with acid. Redwood recommends 4 parts black antimony sulphide, 8 lime, and 80 water, digested, filtered, and precipitated with hydrochloric acid ; or, 2 sulphide, 4 potassium carbonate, and 1 sulphur, to be fused, treated with 20 parts water, filtered, and the solution precipitated with a large excess of sulphuric acid.

On treating the mother liquor from kermes mineral with an acid, the pentasulphide is precipitated with evolution of sulphuretted hydrogen. The mother liquor from Schlippe's salt also yields this substance on the addition of an acid (R. Bartley, Chem. Soc. Trans. 1876, 1, **748**). It generally contains free sulphur.

Antimony pentasulphide is of some import-
ance commercially, as it is used in the process of
vulcanising rubber.

Antimony pentasulphide combines with alka-
line sulphides, forming sulphantimonates, which
as well as the sulphantimonites (which contain
less sulphur) are known as 'livers of antimony.'
Of these the sodium sulphantimonate, or
Schlippe's salt, is the most important. ·

A mixture of 11 parts finely powdered anti-
mony trisulphide, 13 crystallised sodium car-
bonate, 1 flowers of sulphur, 5 recently slaked
lime, and 20 water, is digested at the ordinary
temperature for 24 hours with frequent
stirring, in a vessel which can be closed. It is
then strained and washed several times with
water, the solution and washings are evaporated
in a porcelain or clean iron dish until a sample
yields crystals on cooling; the solution is then
cooled, and the resultant crystals washed with
cold water and dried in the open air or in a
desiccator at the ordinary temperature. The
salt is more rapidly formed when the mixture is
heated (Liebig, Handwörter. d. Chem. 2te Aufl.
2, 139; also Gm. 4, 384).

Oxysulphides of antimony are formed by the
combination of the sulphides and oxides or by
the partial oxidation of the sulphides.

Antimony crocus or saffron. Fuse together
3 parts antimony trioxide and 1 part trisul-
phide, or fuse the oxide with the calculated
quantity of sulphur.

The scoria from the fusion of the sulphide
with carbon and alkaline carbonate in the pre-
paration of the metal is known as crocus of
antimony.

Crocus of antimony is a brownish-yellow
body.

Glass of antimony. Vitrum antimonii. When
antimony sulphide is fused until the necessary
amount of sulphide has been converted into
oxide, the whole forms a glassy mass of this
compound. The best method of preparation is
to roast the sulphide completely into oxide and
fuse the product with $\frac{1}{20}$ part of sulphur. Its
colour varies with the proportion of sulphur
present from yellowish-red to hyacinth red. The
best quality is of a fine red colour, and con-
tains 8 antimonious oxide and 1 antimonious
sulphide.

Antimony cinnabar is an oxysulphide of a
fine vermilion colour, soft and velvety, and un-
altered by air or light; it is used in the prepara-
tion of oil and water colours, and in calico-print-
ing. It is prepared by dissolving antimony
oxide in hydrochloric acid, and placing the solu-
tion in a large wooden tub which is $\frac{2}{3}$ filled
with calcium hyposulphite. The mixture is
stirred and heated with steam to 70°, the pre-
cipitate soon subsides as a yellowish sediment
which changes to a bright orange-red, and is
thoroughly washed, and dried below 50°. N.
Teck (Chem. Zentr. 26, 1880) prepared it from
4 parts tartar emetic, 3 tartaric acid, 18 water
mixed at 60° with hyposulphite of soda and
heated to 90° (Wagner), or 4 volumes antimonious
chloride of sp.gr. 1·19 mixed with 10 vols. water
and 10 vols. hyposulphite of 1·19 sp.gr., and
heated gradually to 55° (Mattieu Blessy).

Antimony yellow (Mérimée's yellow). Accord-
ing to the method of Mérimée, a mixture of 3
parts bismuth, 24 parts antimony sulphide, and

64 parts nitre, is thrown little by little into
a heated crucible, fused, powdered, washed, and
dried. In this way bismuth antimonate is pro-
duced. Of this 1 part is mixed with 8 parts
ammonium chloride and 128 parts litharge, and
fused as before. The time occupied and the
temperature used cause considerable variations
in the colour. Mérimée's yellow is a fine per-
manent colour of good body. It is only used
for the finest painting.

Naples yellow is essentially an antimonate
of lead containing excess of lead oxide, but
mixtures of carbonate and chromate of lead are
also sold under the name. Many processes may
be used for its preparation. According to
Brunner, a mixture of 1 part tartar emetic, 2
parts lead nitrate, and 4 parts sodium chloride is
heated, just to fusion, for 2 hours. The cooled
mass is placed in water and soon falls to pieces.
According to Guimet, it may be produced by
heating a mixture of 1 part potassium antimo-
nate and 2 parts red lead. It is a fine very
permanent orange or yellow pigment, used in
oil-painting, and, mixed usually with a lead glass,
for glass and porcelain staining.

Antimony trichloride (*Butter of antimony*).

Prepared by dissolving the sulphide in strong
hydrochloric acid with a small quantity of nitric
acid and evaporating to dryness.

To prepare the pure chloride, the acid solu-
tion is evaporated until it just crystallises on
standing in a cool place; it is then transferred
to a retort and distilled until a drop of the dis-
tillate solidifies on a cold surface; the receiver
is then changed, and the further distillate is
pure.

It is a white, buttery, semivitreous, delique-
scent solid. When pure, it is crystalline, and
melts sharply at 73·2°, and boils at 223·5°
(Beckmann, Zeitsch. anorg. Chem. 1906, 51, 96).
It is used as a caustic in medicine, for the pre-
paration of tartar emetic, and as a 'bronzing
solution' for gun-barrels, &c. For this pur-
pose a saturated solution is mixed with olive oil,
rubbed over the warmed metal and exposed to
the air until the proper colour is produced.
When bronzed, the metal is polished with a
burnisher or with wax, or coated with a varnish
of 2 oz. shellac, 3 drachms dragon's blood, dis-
solved in 2 quarts of methylated spirit.

Antimony oxychloride. *Basic chloride,
powder of Algaroth; pulvis Algarothi; S.
Argelicus; mercurius vitæ, &c.*

Water is added to a solution of the trichlor-
ide until it is distinctly turbid, when it is filtered
(the precipitate carries down any traces of sul-
phuretted hydrogen which may be present, and
which if left would soon turn the substance
yellow). Five to ten volumes of water are added,
and the precipitate is washed with cold water
and filtered. Its composition varies with the
temperature at which it is produced and the
amount of water used, varying between $SbOCl$
and, where a very large amount of water has
been used, Sb_2O_3. It is a white powder, and is
principally used for the preparation of pure
antimonious oxide and tartar emetic.

Antimonious oxide Sb_4O_6. *Trioxide of anti-
mony.* If antimony is powdered and heated in
a shallow dish, it eventually forms antimony
tetroxide Sb_2O_4; this, together with the un-
changed metal, is fused in a crucible, when

the tetroxide and antimony react, forming antimonious oxide, the excess of antimony sinking to the bottom of the crucible.

For pharmaceutical purposes 20 parts of finely powdered antimony sulphide are gradually added to 100 parts hydrochloric acid containing 1 part nitric acid, and heated, gently at first, and then more strongly, until sulphuretted hydrogen ceases to be evolved. It is then boiled for an hour, enough water is added to produce a slight precipitate, which removes the last traces of sulphuretted hydrogen, and filtered into a vessel containing 1 gallon of water, precipitating the oxychloride, which is filtered and washed until it ceases to have an acid reaction ; it has then become converted into the trioxide.

It is a white fusible solid, slightly soluble in water, volatile at a red heat. It becomes further oxidised to the tetroxide Sb_2O_4 on heating in air, and is then non-volatile.

In presence of alkalis it absorbs oxygen ; for this reason it has been proposed to use it for reducing nitrobenzene to aniline, and in the preparation of aniline red.

It is used for the preparation of tartar emetic. When ground with linseed oil it is sometimes used as a substitute for white lead, being less injurious to the workmen and less acted upon by sulphur gases ; it has, however, less ' body ' and is more expensive.

Tartar emetic. *Potassium antimony tartrate. Tartarus stibiatus. Brechweinstein ; spiessglanzweinstein.* $2C_4H_4K(SbO)O_6,H_2O$. Three parts antimonious oxide and 4 cream of tartar are made into a thin paste with water and digested for about half an hour, keeping the water at constant volume ; 8 parts of water are then added, boiled, and filtered whilst hot. The oxychloride or oxysulphide may be substituted for the oxide, but not so satisfactorily.

Tartar emetic forms octahedral crystals, which give off a part of their water on exposure to the air. They dissolve in 14·5 parts cold and in 1·9 parts boiling water. They show an acid reaction with litmus, and have a nauseous metallic taste, 5–10 centigrams causing vomiting, and larger quantities being very poisonous.

It is used in medicine and in the preparation of pomades, &c., and also largely as a mordant in dyeing and calico-printing. Mixtures of tartar emetic for mordanting are sold containing as much as 33–59 p.c. zinc sulphate at a lower price, under the names *tartar emetic powder, tartar emetic substitute, antimony mordant,* &c. It is known that zinc acetate may partly replace the tartar emetic with advantage, but the sulphate appears to be a simple adulterant (H. Smid, Chem. Zeit. 1882, 949).

Several other compounds of antimony have been proposed for mordants instead of tartar emetic. E. Jacquet (Dingl. poly. J. 257, 168) advised the use of a mixture of basic antimony oxalate with twice its weight of ammonium oxalate. Nölting recommended the double oxalate of potash or of ammonia and antimony (Dingl. poly. J. [3] 255, 122). It is stated that the latter compounds have long been used under other names.

The use of the fluoride (which is not precipitated with excess of water) and the double fluorides of antimony and the alkalis has been patented by S. M'Lean. Watson, jun., patented

a process for using trichloride with sufficient common salt to prevent the precipitation of the oxychloride (G. Watson, J. Soc. Chem. Ind. 1886, 5, 591 ; B. W. Gerland, J. Soc. Chem. Ind. 1884, 4, 643 ; and Kopp and Bruère, J. Soc. Chem. Ind. 1888, 566). A double salt of antimony fluoride and ammonium sulphate SbF_3 $(NH_4)_3SO_4$, known as ' antimony salts,' is also used in dyeing, but as it attacks glass as well as metal, it should be stored and worked in wooden vessels. A good bath is 100 litres water, 400 grams antimony salts, 200 grams soda crystals, at a temperature of 50° (Frey, Bull. Soc. Md. Mulhouse, 1888, 301).

Tartar emetic as a mordant has, at the present time, been largely superseded by the double oxalate of potassium and antimony, as it is cheaper than the tartrate, and equally efficient, although it contains less antimony.

Recently F. Düring has recommended the use of the double lactate of antimony and calcium, which can readily be obtained by mixing, in the dry state or in solution, alkali lactates with ' antimony salts,' or other antimonious compounds (Färber, Zeit. [20] 319). He states that at least 80 p.c. of the antimony in the solution will actually go into the cloth as mordant.

ANTIMONY SALTS. A compound of antimony fluoride with ammonium sulphate used as a mordant (*v.* ANTIMONY).

ANTINONIN. Trade name for a solution of potassium *o*-dinitrocresol used as a fungicide.

ANTIPYRINE. *Phenyldimethylpyrazolone* (*v.* PYRAZOLE).

ANTIRRHINIC ACID *v.* DIGITALIS.

ANTISEPTICS *v.* DISINFECTANTS.

ANTISEPTINE. Said to be a mixture of zinc iodide, zinc sulphate, boric acid, and thymol.

ANTISEPTOL. *Cinchonidine iodosulphate,* used as a substitute for iodoform.

ANTITHERMIN. *Phenylhydrazone of lævulic acid* $CH_3\cdot C(N_2H\cdot C_6H_5)\cdot CH_2\cdot CH_2\cdot CO_2H$ is obtained by dissolving phenylhydrazine in dilute acetic acid, adding an aqueous solution of the equivalent quantity of lævulic (acetopropionic) acid, and crystallising the resulting yellow precipitate from alcohol (Farbw. vorm. Meister, Lucius & Brüning in Höchst a. M., Ger. Pat. 37727).

It forms colourless, inodorous, and tasteless scales, melts at 98°–99°, is sparingly soluble in cold water, soluble in alcohol, ether, or dilute acids. It has been employed as an antipyretic (Nicot, Chem. Zentr. 1887, 415) ; but, according to Stark (Chem. and Drug, 32, 651), its use in medicine is now almost abandoned. Inasmuch as it is decomposed by alkalis, its physiological activity is probably due to phenylhydrazine (Gehe & Co., Chem. Zentr. 1888, 49).

ANTWERP BROWN *v.* PIGMENTS.

ANVULA *v.* AMLAKI.

AOOD-I-BALSAM. *Balsaam of Mecca* (*v.* OLEORESINS).

APATITE. A crystallised mineral, consisting of calcium phosphate in combination with fluorine, chlorine, hydroxyl, or carbonic acid, the formula being $(CaF)Ca_4(PO_4)_3$ or $3Ca_3(PO_4)_2$ + CaF_2, where F may be replaced by Cl, OH, or CO_3. There are thus several chemical varieties, namely, fluor-apatite, chlor-apatite, hydroapatite, and carb-apatite ; the last being also

called podolite (W. Tschirwinsky, 1907). Similarly, by partial replacement of the calcium, there are the chemical varieties mangan-apatite, cupro-apatite, and talc-apatite. In addition to these, some other trivial names are applied to varieties of crystallised apatite ; for example, asparagus-stone, from Murica in Spain ; moroxite, from Arendal in Norway ; and francolite, from Wheal Franco, near Tavistock in Devonshire. The distinction between fluor-apatite and chlor-apatite is, however, the only one of any importance. (For the varieties of massive apatite, *v.* PHOSPHORITE.)

Apatite is often found as well-developed crystals. These belong to the hexagonal system, and are usually bounded by a six-sided prism and pyramid with the basal plane, though sometimes numerous other brilliant facets are present. The colour is commonly greenish or brownish, but sometimes sky-blue, violet, or colourless. The crystals may be transparent or opaque, and they have a vitreous to sub-resinous lustre. Sp.gr. 3·2 ; hardness 5 (the mineral can be scratched with a knife). Owing to its variable appearance, apatite is frequently mistaken for other minerals, and it well deserves its name, from ἀπατᾶν, ' to deceive.' In determining the mineral, it is always well to test for phosphoric acid.

As microscopic crystals, apatite is present as an accessory constituent of igneous rocks of all kinds. It also occurs in metamorphic rocks and in metalliferous veins. Fine specimens are found at many localities, but only in two regions—in Norway and Canada—is crystallised apatite mined for commercial purposes. In southern Norway, in the neighbourhood of Kragerö and Bamle, extensive deposits of chlor-apatite occur in connection with gabbro (a pyroxene-felspar rock of igneous origin). Large deposits of fluor-apatite are mined in Ottawa Co., Quebec, and in Renfrew Co., Ontario ; here the mineral forms beds in Laurentian gneiss, usually in association with crystalline limestone.

L. J. S.

APERITOL. A mixture of equal parts of valerianyl and acetylphenolphthaleïn, used as a laxative.

APHTHITE. An alloy containing 800 parts of copper, 25 of platinum, 10 of tungsten, and 170 of gold (Zeits. f. d. C. Grossgew. 4, 313).

APIGENIN *v.* FLAVONE.

APIIN. A glucoside contained in parsley and celery, forming on hydrolysis *apigenin* and a disaccharide, made up of *α*-glucose and a pentose, *apiose* (Vongerichten, Annalen, 1901, 121), (*v.* FLAVONE and GLUCOSIDES).

APIOL *v.* OILS, ESSENTIAL.

APIOSE *v.* CARBOHYDRATES.

APIOS TUBEROSA (Moench.), *Glycine apios* (Linn.). A leguminous plant from North America, the roots of which have been proposed as a substitute for the potato, and the young seeds for peas. Payen (Compt. rend. 28, 189) gives the following analysis of the root : Nitrogenous matters, 4·5 ; fatty matters, 0·8 ; starch, sugar, &c., 33·55 ; cellulose, &c., 1·3 ; inorganic, 2·25 ; water, 57·8 (*cf.* Brighetti, Chem. Zentr. 1900, i. 914).

APIUM *v.* OILS, ESSENTIAL.

APIUM PETROSELINUM (*Carum petro- v.* FLAVONE.

APOLLO RED *v.* AZO- COLOURING MATTERS.
APOMORPHINE *v.* VEGETO-ALKALOIDS.
APOPHYLLITE *v.* CALCIUM.
APOREINE. A poisonous alkaloid found in juice of *Papaver dubium.* Gives crystalline salts. The hydrochloride $C_{18}H_{16}NO_3$.HCl, forms silvery nacreous scales, subliming without decomposition in dry carbon dioxide between 220° and 240°.

APORETIN *v.* RHUBARB.

APOTURMERIC ACID *v.* TURMERIC.

APPLE. The fruit of *Pyrus malus.* Many varieties are known, differing greatly in size, ype, colour, and flavour.

The solid matter of apples consists largely of sugars—glucose and sucrose ; their acidity is due to malic acid $C_2H_4O(COOH)_2$. In unripe apples starch is present—sometimes to the extent of 4 or 5 p.c., but the fully ripened fruit is devoid of starch. Cellulose forms about 1 p.c. of the weight of the ripe fruit, pentosans about 0·5 p.c., and pectose matters also about 0·5 p.c. Mineral matter is usually between 0·2 and 0·3 p.c., and about half of this is potash.

The following analyses of American Baldwin apples show the changes which occur during ripening :—

	Very green	Green	Ripe	Over-ripe
Water	81·33	79·81	80·36	80·30
Solids	18·67	20·19	19·64	19·70
Reducing sugars .	6·40	6·46	7·70	8·81
Cane sugar .	1·63	4·05	6·81	5·26
Starch	4·14	3·67	0·17	none
Free malic acid .	1·14	—	0·65	0·48
Ash .	0·27	—	0·27	0·28

The following figures relate to South-African apples (Ingle). The flesh and rind of the ripe fruit, the core and pips being rejected, contained :—

Variety	Koo	Rei-nette de Canada	Nor-thern spy	Vers-feld	Lord Wolse-ley
Water .	85·08	—	82·64	87·65	84·41
Dry matter .	14·92	—	17·36	12·35	15·59
Ash .	0·313	—	0·262	0·270	0·268
Acidity (as malic acid) .	0·47	0·65	0·48	0·71	0·47
Reducing sugars	7·44	6·87	10·26	9·43	10·85
Cane sugar	4·63	3·68	4·77	1·36	1·58
Nitrogen .	0·046	0·094	0·058	0·057	0·043
Crude fibre .	1·33	1·24	1·26		0·88
Per cent. in ash :					
Potash .	54·48	—	48·52	53·30	51·58
Lime .	2·63	—	1·95	1·82	2·70
Silica .	1·51	—	1·58	1·25	0·90
Phosphorus pentoxide.	11·15	—	12·10	8·09	12·16
Sulphur tri-oxide .	2·46	—	2·67	3·13	3·10
Chlorine .	0·50	—	0·89	1·02	1·00

The proportions of lime found in these apples are apparently lower than those usually found

in American apples, while the figures for phosphorus pentoxide and chlorine are higher.

Hotter (Chem. Zentr. 1900, ii. 484) gives the following analysis of apple ash :—

K_2O	CaO	MgO	Fe_2O_3	SiO_2	SO_3	P_2O_5
51·58	4·22	3·71	1·18	1·08	2·49	10·42

Certain varieties of apples—particularly those used for cider-making—are rich in tannin, and, when the cells are broken, e.g. by cutting the apple or by a bruise, so as to admit air, a browning takes place—probably by the action of an oxydase upon the tannin.

Otto (Bied. Zentr. 1901, ii. 553 ; and 1902, 31, 107) found that the percentage of water increases during ripening on the tree, but diminishes on storing, that the starch diminishes and finally disappears, while the cellulose remains constant. The nitrogen increases during ripening on the tree, but afterwards diminishes. The acidity diminishes during ripening, both before and after gathering.

Under normal conditions, the starch present in unripe apples is converted, during ripening, into sugar by the diastase present, but if the unripe apples be bruised, this change is incomplete in the bruised portion, and starch may be found in the browned tissues. According to Warcollier (Compt. rend. 1905, 141, 405), this is due to the paralysing effect upon the diastase of the tannin which escapes from the bruised cells (and which, by the action of an oxydase, gives rise to the browning), thus preventing the saccharification of the starch, upon which normal ripening depends.

Apples are now dried by artificial heat (with or without the use of sulphur dioxide, which improves the colour), and sold, either as whole fruit or as 'apple rings.' Fresh apples yield about one-seventh of their weight of the dried product. Zinc is frequently found in dried apples, probably from contact with zinc trays during the drying process. As much as 0·58 gram Zn per kilogram has been found in American dried apples. American analyses give as the average components of dried apples : 36 p.c. water, 1·4 p.c. protein, 3·0 p.c. ether extract, 57·6 p.c. carbohydrates, and 1·8 p.c. ash. The flavour, and particularly the odour, of apples can be imitated by iso-amyl-iso-valerate dissolved in spirits of wine. This constitutes the 'essence of apples' used in confectionery and perfumery.

H. I.

APPLES, ESSENCE OF, v. APPLES.

APPLE TREE. (*Pyrus malus*, L. ; *Pomme*, Fr. ; *Apfel*, Ger.) The wood is much used in turnery, and that of the crab tree is used by millwrights for the teeth of mortice wheels. The bark contains a tannin identical with that contained in horse-chestnut bark.

APRICOT. The fruit of *Prunus armeniaca* (Linn.).

The following analyses were made by Fresenius :—

	I. Medium	II. Large wt. 60 grams.
Sugars	1·14	1·53
Soluble { Free acid	0·90	0·77
Nitrogenous matter.	0·83	0·39
Pectins, gum, &c.	5·93	9·28
Ash	0·82	0·75
Total soluble matter	——9·62	12·7

Insoluble { Seeds (stone)	4·30	3·22
Skin and cellulose	0·97	0·94
Pectose	0·15	1·00
Ash	(0·07)	(0·10)
Total insoluble matter, excluding ash	——5·42	——5·16
Water	84·96	82·12
	100·00	100·00

In Californian-grown apricots, Colby (Exp. Stat. Record, 1893, 1, 91s, found, in the whole, fresh fruit, water, 85·16 ; dry matter, 14·84 ; containing nitrogen, 0·194 ; sugar, 11·10 ; ash, 0·49.

The ash was found to contain :

K_2O	Na_2O	CaO	MgO	MnO_2	P_2O_5	SO_3	SiO_2
59·36	10·26	3·17	3·68	0·37	13·09	3·63	5·23

Cl	Fe_2O_3
0·45	1·68

Californian apricots appear to contain more nitrogen than the European fruit. As many other analyses agree in giving about 11 p.c. of sugar, it is probable that some error has been made in Fresenius' figures, though they have been widely quoted.

The sugar is chiefly sucrose, with a little dextrose, and invert sugar, which becomes less when the fruit ripens (Desmoulière Ann. Chim. anal. 1902, 7, 323). The colouring matter is probably related to carrotene.

The acidity of apricots is chiefly due to malic and citric acids.

The kernels of apricot 'pits,' or stones, like those of the other members of the *Prunus* family, contain amygdalin and about 40 p.c. of a fatty oil resembling almond oil. This oil has a sp.gr. of 0·9204 at 15·5°, a pale-yellow colour, and a slight odour of almonds (Maben, Pharm. J. Trans. [3] 16, 797). More recent determinations give the following (Dieterich, Chem. Zentr. 1902, 2 [15], 943) : sp.gr. at 15°C. 0·915–0·921, at 90°, 0·9010–0·9015 ; solidifying point, −14° to −20° ; saponification value, 193·1–215·1 ; iodine value (Hübl), 100–108·7 ; refractometer value at 25°, 65·6–67·0 ; at 40°, 58·0 ; at 50°, 52·25. It can be distinguished from almond oil by Biber's reagent (fuming nitric acid, sulphuric acid and water), with which it gives a red colour, while almond oil only yields a faint yellow.

The flavour of apricots can be imitated by a mixture of isoamyl butyrate and isoamyl alcohol.

Dried apricots are prepared either by sundrying or by artificial heat, sulphur dioxide being often employed in the latter case, in order to prevent darkening in colour. They are largely used in America and in some of the colonies. American analyses show them to contain about 32 p.c. of water, 63 p.c. of carbohydrates, 2·9 p.c. of nitrogenous matter, and 1·4 p.c. of ash.

H. I.

APRICOT, ESSENCE OF. A mixture of isoamyl butyrate and isoamyl alcohol.

APRICOT KERNEL OIL v. ALMOND OIL.

AQUA FORTIS v. NITRIC ACID.

AQUA REGIA. *Nitromuriatic acid ; Königswasser.* A name given by the alchemists to a mixture of nitric and hydrochloric acids, originally prepared by dissolving sal ammoniac in strong nitric acid, and used by them as a solvent for gold, sulphur, &c. Usually made

by mixing 1 vol. of nitric acid with 4 vols. of hydrochloric acid. The mixture is at first colourless, but gradually—especially on heating —acquires a deep orange-yellow colour, due to the formation of nitrosyl chloride and free chlorine : $HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$. The solvent action of aqua regia appears to be mainly due to the free chlorine.

AQUA VITÆ. An alchemistic name used to denote common alcohol as obtained by distilling a liquid which has undergone vinous fermentation.

ARABIC GUM *v.* Gums.

ARABINOSE *v.* Carbohydrates.

ARACHIDIC ACID $CH_3(CH_2)_{18}COOH$ is found partly free and partly as a glyceride in earth-nut oil (from *Arachis hypogæa* (Linn.)) ; in butter, and in the fruit of *Nephelium lappaceum* (Heintz. Pogg. 90, 146 ; Grössmann, Annalen, 89, 1 ; Oudemans, Zeits. f. Chem. 1867, 256). It has been prepared by treating behenolic acid $C_{22}H_{40}O_2$ with fuming nitric acid (Grössmann, Ber. 1893, 644), and synthetically from aceto-acetic ester and octodecyl iodide (Schweizer, Arch. Pharm. 1884, 753) ; m.p. 77° (Baczewski, Monatsh. 17, 530).

ARACHIS OIL is obtained from the seeds of *Arachis hypogæa* (Linn.), which are known in commerce as earth nuts or monkey nuts. The cultivation of the arachis plant dates back so far in history that its origin is unknown. It is frequently assumed that the home of the arachis nut is Brazil. The plant is chiefly cultivated in the East Indies, Indo-China, Java, Japan, the West Coast of Africa, Mozambique, Madagascar, Egypt, Spain, Sicily, the United States of America, the Argentine, and in the West Indian Islands. The East Indian and West African nuts represent two distinct varieties. In commerce a distinction is made between decorticated and non-decorticated nuts. The Indian and Mozambique nuts are usually decorticated before they are shipped to Europe ; as they undergo some detrimental changes on the voyage, they cannot be used for the production of best edible oil, and are mostly worked up for soap oil. The nuts coming from West Africa mostly arrive non-decorticated, and are therefore suitable for the preparation of best edible oil, the lower qualities only, derived from a second and third expression (*see* below) being used for technical purposes. The approximate composition of arachis nut, taking the average of nuts from various places of origin, is as follows : oil, 38–50 p.c. ; water, 4·6–12·8 p.c. ; albuminoids, 26–31 p.c. ; carbohydrates, 5–19 p.c. ; fibre, 1·1–4·1 p.c. ; ash, 1·6–3·0 p.c.

The undecorticated nuts are shelled by special machinery and the inner red skin which surrounds the kernel is removed as completely as possible by a blast of air. The separated and cleaned kernels are then ground in the usual manner and subjected to hydraulic pressure. As the kernels contain so high a proportion of oil, the expression of the oil is carried out in two stages ; frequently the meal is even expressed three times. The first expression takes place at the ordinary temperature, and yields the 'cold-drawn' oil ; the second expression is carried out at a temperature of 30°– 32° ; and the third expression at 50°–55°.

The 'cold-drawn' oil is nearly colourless, and has a pleasant taste, recalling that of

kidney beans ; it is used as salad oil, and sold under the name 'huile surfine.' The oil obtained by the next expression also serves for edible purposes, in the sardine and margarine industries, or for burning ; the lowest quality, which has been expressed at the highest temperature, is chiefly used for soap-making.

The arachis cakes serve as an excellent cattle food, for they contain the highest amount of proteids of all known oil cakes ; moreover, these proteids are more easily digested than those of other cakes.

On standing a few degrees above freezing-point, 'stearine' deposits from arachis oil. This stearine contains *arachin* which does not settle out as a crystalline mass, so that it cannot be removed in the usual manner by expression. Hence it is necessary, in order to 'demargarinate' arachis oil, to allow it to stand for a prolonged time in the cold, when 'margarine d'arachide' settles out, so that the supernatant clear oil can be drawn off.

Amongst the solid fatty acids of arachis oil, arachidic acid and lignoceric acid have been identified. These two acids are characteristic of arachis oil, and as their proportion can be determined quantitatively, the separation and determination of 'crude arachidic acid' (*i.e.* a mixture of arachidic and lignoceric acids) furnishes an excellent means of identifying arachis oil, and determining its proportion in mixtures with other oils. Amongst the liquid fatty acids of arachis oil, oleic acid undoubtedly predominates ; in addition to it there has also been proved the presence of hypogæic and linolic acids.

Arachis oil has a sp.gr. 0·917–0·919 at 15° ; its iodine value fluctuates between 87 and 100. As the iodine value of arachis oil lies so near that of olive oil, adulteration of olive oil with arachis oil takes place on the largest scale ; indeed, very frequently arachis oil is entirely substituted for olive oil (as in the preparation of tinned sardines).

Arachis oil is chiefly expressed in the South of Europe (Marseilles and Trieste) ; therefore the lower qualities of this oil enter largely into the composition of the soaps of South Europe. Thus, one of the most characteristic components of the Marseilles white soap is arachis oil. The quantity of arachis nuts imported into France during the year 1907 was : arachis nuts in shells, 163,241 tons ; decorticated arachis nuts, 117,404 tons. The total quantity of arachis nuts produced in the world may be taken to amount to about 350,000 tons. Next to France, arachis nuts are largely imported into Trieste, Delft, and in smaller quantities to Germany (about 25,000 tons), and to the United States of America. The latter country produces about 50,000 tons per annum.   J. L.

ARAGONITE. The orthorhombic form of calcium carbonate ($CaCO_3$), differing from the more common dimorphous form calcite (*q.v.*) in its greater density (sp.gr. 2·93), greater hardness (H. 3½), and in the absence of cleavage. It crystallises, together with calcite, from aqueous solutions containing carbon dioxide at temperatures above 18°, and the presence of various salts in the solution favours its growth. In nature it is deposited by thermal springs, for instance, those of Carlsbad in Bohemia, in the form of

pea-like concretions, this variety of the mineral being known as *pisolite*. Another variety, called *flos-ferri* (flower of iron), is found as snow-white coralloidal forms in the iron-mines of Styria. Crystals were first found embedded in red clay and gypsum in Aragon, Spain; and divergent groups of spear-like crystals have been found in an iron (hæmatite) mine in west Cumberland.　　　　　　　　　　　　　　L. J. S.

ARALIA BARK or *False Prickly Ash Bark*, the bark of *Aralia spinosa* (Linn.), contains a volatile oil, an amorphous bitter substance, (tannin), a grey acrid resin, and a glucoside to which the name *araleïn* has been given (Lilly, Pharm. J. [3] 13, 305). By boiling araleïn with dilute hydrochloric acid, *araliretin* is obtained (Holden, Pharm. J. [3] 11, 210; Chem. Soc. Trans. 40, 105).

ARAROBA POWDER. *Goa Powder; Chrys-arobin.* A powder varying in colour from a pale primrose yellow to bronze and purple, which collects, possibly as the result of oxidation of the resin, in the cavities of the stems and branches of the *Andira Araroba* (Aguiar) (ord. *Leguminosæ*), a tree inhabiting the forests of Bahia in Brazil (Aguiar, Pharm. J. [3] 10, 42; cf. Greenish, *ibid.* [3] 10, 814).

Crude araroba was examined by Attfield in 1875 (Pharm. J. [3] 5, 721), and found to contain *moisture*, 1 p.c.; *glucoside, bitter constituent* and *arabin*, 7 p.c.; *yellow crystalline substance* extracted with benzol, supposed to be chrysophanic acid, 80–84 p.c.; *resins*, 2 p.c.; *woody fibre*, 5·5 p.c. On incineration, 0·5 p.c. of *ash* was obtained.

The yellow crystalline compound which constitutes the chief part of Goa powder and to which its activity is probably due, was subsequently examined by Liebermann and Seidler (Ber. 11, 1603; Annalen, 212, 29). It was shown to be *chrysarobin*, independent of, but closely related to, chrysophanic acid, and into which it is readily converted by the oxidising action of the air. This is most expeditiously effected by leading a current of air through Goa powder dissolved in aqueous potash. Hesse (Annalen, 309, 32) finds that araroba powder contains no chrysophanic acid, but is a mixture of chrysarobin $C_{15}H_{12}O_3$, while a substance yielding methyl iodide by Zeisel's method, which was assumed by Hesse to be chrysarobin methyl ether.

Araroba powder has been fully investigated by Jowett and Potter (Chem. Soc. Trans. 81, 1575), who have isolated the following substances: *chrysarobin* $C_{15}H_{12}O_3$; *dichrysarobin* $C_{30}H_{24}O_7$; *dichrysarobin methyl ether* $C_{31}H_{26}O_7$, melting at 160°; and a substance, $C_{17}H_{14}O_4$, m.p. 181°.

Pure chrysarobin prepared from the commercial product by extraction with light petroleum, distilling, and recrystallising the residue repeatedly from a large quantity of ethyl acetate, consists of lemon-yellow scales melting at 202° (corr.) insoluble in aqueous sodium carbonate, but soluble in caustic alkalis, giving a yellow solution which becomes red in the air. It dissolves in concentrated sulphuric acid with a yellow colour. On distillation with zinc, β-methyl anthracene is obtained. When acetylated, chrysarobin yields a diacetyl compound, $C_{15}H_{10}O_3Ac_2$, m.p. 193°, and a triacetyl compound, $C_{15}H_9O_3Ac_3$, m.p. 238°. A minute quantity (1 mg.) of chrysarobin sprinkled on a

drop of fuming nitric acid gives a red solution, which when spread in a thin layer and treated with ammonia strikes a violet colour (Pharm. Germ.).

Dichrysarobin consists of orange crystals, decomposing at about 250°. It is distinguished from chrysarobin by being insoluble in benzene; it also appears to be more readily oxidised, yielding, similar to chrysarobin, chrysophanic acid. A hexa-acetyl derivative, $C_{30}H_{18}O_7Ac_6$, m.p. 178°–181°, has been obtained, and on distillation with zinc-dust β-methyl anthracene is formed.

Though sometimes administered internally as a purgative, araroba powder is used in medicine almost exclusively as an external remedy in the form of ointment, in the treatment if certain skin diseases.　　　　　　　　A. S.

ARASINA GURGI. An impure gamboge from Camara, obtained probably from a species of Garcinia (Dymock, Pharm. J. [3] 7, 451).

ARBOL-A-BREA RESIN is obtained from *Canarium luzonicum* (Miq.), a tree belonging to the Burseraceæ, growing in the Philippines. The resin is greyish-yellow, soft, glutinous, and has a strong agreeable odour. It contains 61·29 parts of resin very soluble in alcohol; 25·00 parts of resin sparingly soluble in alcohol; 6·25 essential oil; 0·52 free acid; 0·52 bitter extractive matter; 6·42 woody and earthy impurities (Bonastre, Jour. Pharm. 10, 129). Baup has isolated four crystalline substances, *Amyrin, Breïdin, Breïn*, and *Bryoïdine* (Ann. Chim. Phys. [3] 31, 108).

ARBUTIN *v.* GLUCOSIDES.

ARCHIL or **ORCHIL** (*Orseille*, Fr.; *Orseille*, Ger.; *Oricello*, It.) appears in commerce in three forms: (1) as a pasty matter called *archil*; (2) as a mass of a drier character, named *persis*; and (3) as a reddish powder called *cudbear*. It is obtained from various lichens of the genus Roccella, growing on the rocky coasts of the Azores, the Canaries and Cape de Verd Isles, also of the Cape of Good Hope, Madeira, Corsica, Sardinia, &c., and from *Ochrolechia tartarea*, growing in Sweden and Norway. None of these lichens contains the colouring matters ready formed, but they contain certain colourless acids of the type of *lecanoric acid*, derivatives of orcin, into which they can be readily converted. Thus, lecanoric acid (1) gives first orsellenic acid; (2) and subsequently orcin (3) according to the following scheme. (*See* under LECANORIC ACID.)
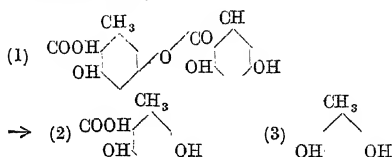
Orcin itself, when acted upon by air and ammonia, changes into a purple substance called *orcein*, which is the name applied to the colouring matters of archil (Robiquet, Ann. Chim. Phys. [2] 47, 238).

Finely powdered orcin is placed in a thin layer under a bell jar, together with a beaker containing strong ammonia solution. As soon

as the substance has become brown-coloured, it is removed and exposed to air for some time. It is then dissolved in very dilute ammonia solution, reprecipitated with acetic acid, and dried. According to Gerhardt and Laurent, orcin has the composition $C_{14}H_7NO_6$ (Ann. Chim. Phys. [3] 24, 315), but more recent researches indicate that it is a mixture of substances. Liebermann, for instance (Ber. 7, 247 ; 8, 1649), considers that by this re-action three colouring matters are produced, having respectively the formulæ (a) $C_{14}H_{13}NO_4$; (b) $C_{14}H_{12}N_2O_3$; and (c) $C_{14}H_{12}N_2O_3$.

Zulkowski and Peters (Monatsh, 11, 227) allowed orcin to remain in contact with ammonia for two months, and from the product isolated three substances:

(a) *Red orcein* $C_{28}H_{24}N_2O_7$, the main pro-duct, which appears to be formed according to the following equation :—

$$4C_7H_8O_2+2NH_3+6O=C_{28}H_{24}N_2O_7+7H_2O.$$
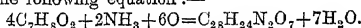
It is a brown crystalline powder, soluble in alcohol with a red colour, and in alkaline solu-tions with a blue-violet tint.

(b) A crystalline yellow compound,$C_{21}H_{19}NO_5$, which is accounted for as follows :—

$$3C_7H_8O_2+NH_3+3O=C_{21}H_{19}NO_5+4H_2O.$$
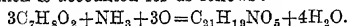
(c) An amorphous product similar to litmus.

These substances can be prepared much more rapidly by the addition of hydrogen peroxide to an ammoniacal solution of orcin.

There can be no doubt that this reaction proceeds in several stages, and that the cha-racter of the product varies according to the duration of the process. This is well known to manufacturers, who can prepare at will a blue or a red orchil. The constitution of these colouring matters has not yet been determined, but in view of the circumstances by which they are produced, it is most probable that they are members either of the *oxazine* or *oxazone* groups.

Orchil was originally prepared from the lichens by means of stale urine, which supplied the necessary ammonia, but ammonia solution is now exclusively employed. The older methods have, however, been greatly improved, and in the place of barrels the operation is carried out in large horizontal or vertical cylinders fitted with stirrers, and suitable openings for the admission of air.

In such an apparatus the weed is digested with about three times its weight of ammonia solution at 60° for from three days to one week, the admission of air being regulated according to the judgment of the manufacturer. The first product of the reaction has a blue colour, and if the process be stopped at this point, there is formed the dyeware known as *blue orchil*. On the other hand, if the action of the air and ammonia is allowed to proceed further, *red orchil* is obtained. These orchil pastes when dried and finely ground, constitute the product known as *cudbear*.

Bedford (Ger. Pat. 57612, 1889) blows air or oxygen through the ammoniacal mixture, which, especially in the latter case, materially shortens the process. The apparatus employed is erected vertically, and by an ingenious arrangement of projecting shelves, the edges of which are turned down, a considerable quantity

of the air or oxygen is entrapped, and exerts therefore a more powerful oxidising effect.

Orchil liquor is prepared by extracting the lichens with boiling water, concentrating the extract to from 8 to 10°Tw., and submitting this to the action of air and ammonia; whereas *orchil extract* is produced by the extraction of orchil paste itself.

In former times archil and cudbear were frequently adulterated with magenta, certain azo-colours, extracts of logwood, brazilwood, &c.; but as the importance of these dyestuffs has now very greatly diminished, such a contamina-tion is at the present time of rare occurrence.

Archil and its preparations are substantive colouring matters, which dye well in a neutral bath, but have the useful property of behaving nearly as well under slightly acid or alightly alkaline conditions. Even colours of con-siderable intensity are produced from it without difficulty, but unfortunately these are not fast to light. Wool is dyed in a neutral bath, or with addition of a trace of sulphuric acid, and silk is dyed in the presence of soap solution, acetic acid being sometimes added. Archil is not applied to cotton.

Archil was at one time employed to a large extent for ' bottoming ' indigo, that is to say, the fabric was first dyed with archil and subse-quently with indigo. The reverse process, known as ' topping,' has again been considerably in vogue. Cudbear and archil are also used to a limited extent in conjunction with other dyestuffs for the production of compound shades. White wines are sometimes coloured with archil, but its presence can be detected by precipitating with lead acetate and extracting with amyl alcohol, when a red colour indicates the presence of archil or magenta. The addition of a little hydrochloric acid changes the colour to yellow if magenta be present, but does not alter it if archil is the adulterant (Haas, Zeitsch. anal. Chem. 20, 869 ; J. Soc. Chem. Ind. 1, 119).

A. G. P.

ARCHIL REDS v. AZO- COLOURING MATTERS.

ARCHIL SUBSTITUTES v. AZO- COLOURING MATTERS.

ARECA. A genus of palms containing the important species *Areca Catechu* (Linn.) (*betel nut* or *areca nut*), the fruit of which is used as a masticatory in the East Indies. It contains an inferior catechu, tannic and gallic acids, am-monium acetate, fats, oils, gum, nitrogenous substances, and a dye (*areca red*). The charcoal of the nut is used as a tooth powder, and the ground nut is employed as a remedy for tape-worm.

AREOMETER v. HYDROMETER.

ARGAL v. ARGOL.

ARGAN OIL. An oil obtained from the kernels of *Argania Sideroxylon* (Roem. et Schult) (ord. *Sapotaceæ*), growing in Morocco. The kernels are first roasted, ground to powder and mixed with water, when the oil separates (Pharm. J. [3] 10, 127).

ARGENTAN. *Aluminium bronze* (v. ALU-MINIUM).

ARGENTINE. A name given by R. Kirwan in 1794 to a variety of calcite ($CaCO_3$) occurring as small scales with a pearly white or silvery lustre.

ARGENTINE. Finely divided spongy tin,

made by reducing a weak solution of tin salt (120 grams in 60 litres of water) by zinc. The tin is collected in a sieve, washed with water, and dried at a gentle heat. Used for tin-plating and also for printing upon fabrics and paper (Deut. Ind. Zeit. 23, 255 ; J. Soc. Chem. Ind. 7, 504).

ARGENTITE. A mineral consisting of silver sulphide Ag_2S, and occurring as cubic crystals or as compact masses. It is blackish lead-grey in colour, and perfectly sectile ; surfaces cut with a knife are bright and shining. Containing 87·1 p.c. of silver, it is a valuable ore of the metal when met with in quantity, as in the Comstock lode in Nevada and in Mexico.

L. J. S.

ARGENTOL. A synthetic antiseptic, consisting of a compound of silver, with quinosol, of the formula $C_9H_5N(OH)SO_3\cdot Ag$. Forms a yellowish powder, of a faint smell, sparingly soluble in water and alcohol (Pharm. Zeit. 1897, 42, 243).

ARGENTORAT. Trade name for a flash-powder consisting of a mixture of potassium perchlorate and aluminium, used in photography : gives very little smoke (v. FLASH-POWDERS).

ARGINASE. An enzyme occurring in the liver, also present in the kidney, the intestinal mucous membrane, thymus, and other organs (Kossel and Dakin, Zeitsch. physiol. Chem. 1904, 41, 321), and found by Shiga (Zeitsch. physiol. Chem. 1904, 42, 502) among the enzymes obtained from yeast ; it can be extracted from the liver by water or dilute acetic acid, and is precipitated from solution by alcohol, ether, or ammonium sulphate. Arginase is a specific enzyme for the exclusive hydrolysis of d-arginine or of substances containing the d-arginine grouping, which it converts almost quantitatively into carbamide and d-ornithine. Creatine and other guanidine derivatives structurally similar to arginine, or guanidine itself, are incapable of hydrolysis by this enzyme (Dakin, J. Biol. Chem. 1907, 3, 435).

ARGININE $C_6H_{14}O_2N_4$, a-amino-δ-guanido-n-valeric acid NH : C(NH₂)·NH·CH₂·₃·CH·NH₂· CO₂H, first isolated by Schulze and Steiger (Ber. 1886, 19, 1177) from the etiolated germinated cotyledons of Lupinus, is the most widely distributed dissociation product of proteid matter, and can be obtained by hydrolysis of the proteid matter of seeds of Lupinus luteus, Cucurbita pepo, Picea excelsa, to the extent of 10 p.c., Abies pectinata, Pinus sylvestris, and other conifers (Schulze, Ber. 1891, 24, 276 ; Zeitsch. physiol. Chem. 1896, 22, 411, 435 ; 1897, 24, 276). According to Suzuki (Chem. Zeit. 1899, 23, 658) the arginine obtained from the seeds of conifers exists already formed, but in loose combination with the proteid material, and is also produced synthetically in the plant from ammonium salts and nitrates, either in full or diffused daylight (Bull. Coll. Agr. Tokyo Imp. Univ. 1900, 4, 25). Arginine is also one of the constituents of the product of hydrolysis of proteids of animal origin, thus, horn yields 2·25 p.c. ; glue, 2·60 p.c. ; conglutin, 2·75 p.c. ; albumen from yolk of egg, 2·3 p.c. ; from white of egg, 0·8 p.c. ; blood serum, 0·7 p.c. ; and

VOL. I.—T.

casein, 0·25 p.c. (Hedin, Zeitsch. physiol. Chem. 1894, 20, 186), whilst the protamines salmine, sturine, Clupeine, Scombrine, Cyclopterine, and Crenilabrine yield arginine as the chief product of hydrolysis (Kossel, Zeitsch. physiol. Chem. 1896, 22, 176 ; 1898, 25, 165 ; 1899, 26, 588 ; 1904, 40, 565 ; 1910, 69, 138). In cases of phosphorus-poisoning arginine is found in the urine (Wohlgemuth, Zeitsch. physiol. Chem. 1905, 44, 74), whilst the amount obtained from the liver is diminished (Wakeman, Zeitsch. physiol. Chem. 1908, 44, 335).

When arginine is heated with barium hydroxide, it is decomposed into ammonia, carbamide, and ornithine (q.v.) (aδ-diaminovaleric acid); cyanamide reacts with ornithine at the ordinary temperature to form arginine (Schulze and Winterstein, Zeitsch. physiol. Chem. 1898, 26, 1 ; Ber. 1899, 32, 3191), or with a-benzoylornithine to form the benzoyl derivative of arginine, and this is readily hydrolysed to arginine, and is thus proved to be a-amino-δ-guanino-n-valeric acid (Sörensen, Ber. 1910, 43, 643).

Arginine crystallises in brilliant monoclinic plates (Gulewitz, Zeitsch. physiol. Chem. 1887, 11, 53); m.p. 207°–207·5° (Gulewitz, Zeitsch. physiol. Chem. 1899, 27, 178); it also crystallises with $1H_2O$ in rhombohedra (Hedin, Zeitsch. physiol. Chem. 1895, 21, 160); it dissolves readily in water, and is sparingly soluble in alcohol. Arginine contains an asymmetric carbon atom, and the dextrorotatory form is the natural product, the hydrochloride has $[\alpha]_D + 12·5°$ in aqueous or $+25·5°$ in hydrochloric acid solution. Arginine is strongly alkaline, and its solution absorbs carbon dioxide from the air ; it forms well defined crystalline salts with acids, and compounds with certain metallic salts (Gulewitz, l.c.). The nitrate $C_6H_{14}O_2N_4$, $HNO_3, \frac{1}{2}H_2O$ has m.p. 126° ; the dinitrate $C_6H_{14}O_2N_4, 2HNO_3$ has m.p. 151° ; the hydrochloride $C_6H_{14}O_2N_4, HCl, H_2O$ melts and decomposes at 209° when anhydrous ; the silver nitrate compounds $C_6H_{14}O_2N_4, AgNO_3, \frac{1}{2}H_2O$ decomposes at 164°, and $C_6H_{14}O_2N_4, AgNO_3$, HNO_3 melts and decomposes at 180° ; the cupric nitrate compound $2C_6H_{14}O_2N_4, Cu(NO_3)_2$, $3H_2O$ melts at 112°–114° or decomposes at 232°–234° when anhydrous ; the copper sulphate compound melts at 110° or decomposes when anhydrous at 235°–238° ; the picrate $C_6H_{14}O_2N_4$, $C_6H_3O_7N_3, 2H_2O$, m.p. 205°, dissolves in 204·1 parts of water at 16° ; the picrolonate $C_6H_{14}O_2N_4$, $C_{10}H_8O_5N_4, H_2O$, m.p. 231°, dissolves in 1124 parts of water, or 2885 parts of alcohol at the ordinary temperature (Schulze and Steiger, Ber. 1886, 19, 1177 ; Hedin, Zeitsch. physiol. Chem. 1894, 20, 186 ; Gulewitz, ibid. 1899, 27, 178 ; Steudel, ibid. 1903, 37, 219 ; Reisser, ibid. 1906, 49, 210).

Certain acyl derivatives and esters of arginine have also been prepared, the dibenzoyl derivative $C_6H_{12}O_2N_4Bz_2$ crystallises in rhombic needles or prisms, m.p. 217·5°–218° (Gulewitz, l.c.), the β-naphthalenesulphonic derivative $C_6H_{13}O_2N_4 \cdot SO_2 \cdot C_{10}H_7$, is a colourless powder, m.p. 88°–89° (Reisser, l.c.); diarginylarginine is isolated as the dipicrate $C_{18}H_{38}O_4N_{12}(C_6H_3O_7N_3)_2, 2H_2O$, m.p. 207°, from the product obtained by hydrolysing pepsin extract with hydrogen fluoride ;

σ

arginylarginine picrate $C_{12}H_{26}O_3N_8,C_6H_3O_7N_3$, $2H_2O$, m.p. 213°, is similarly obtained from gelatin (Hugouenq and Morel, Compt. rend. 1909, 148, 236); *arginine methyl ester hydrochloride* has m.p. 195° (corr.) with decomposition, the *picrate* forms lemon-yellow crystals, which melt and decompose at 218° (corr.); and the *nitrate* melts at 189° (corr.) (Fischer and Suzuki, Sitzungber. K. Akad. Wiss. Berlin, 1904, 1333).

The presence of arginine assists the tryptic digestion of proteid matter and aids the emulsification of fats : this appears to be connected with its alkalinity, as sodium carbonate acts similarly (Lawroff, Zeitsch. physiol. Chem. 1899, 28, 303). When arginine (hydrochloride or carbonate) is administered as a food, it suffers complete decomposition, and 37–77 p.c. of the nitrogen so given reappears as urea (Thompson, Zeitsch. physiol. Chem. 1905, 33, 106), and the amount of arginine in the various organs shows no increase (Orglmeister, Beitr. Chem. Physiol. Path. 1905, 7, 27).

Arginine is readily oxidised by hot calcium or barium permanganate yielding guanidine, γ-guaninobutyric acid and succinic acid (Bénech, Kutscher, Zeitsch. physiol. Chem. 1901, 32, 278, 413), and the estimation of the number of arginine groups in proteids is based on this reaction (Orglmeister, *l.c.*; Kutscher and Zickgraf, Sitzungsber. K. Akad. Wiss. Berlin, 1903, 28, 624), the guanidine thus obtained being isolated in the form of its sparingly soluble picrate, and either weighed as such, or the nitrogen estimated in the usual way. Another method of isolating and estimating arginine is based on Siegfried's carbamino- reaction of amino- acids (Zeitsch. physiol. Chem. 1905, 44, 85; 46, 402; 1907, 50, 171; Ber. 1906, 39, 397), whereby the barium, strontium, or calcium salt of the corresponding carbamic acid is formed when carbon dioxide is passed into a solution of the amino- acid containing excess of alkali earth hydroxide until the solution is neutral to phenolphthaleïn—

$$RCH \cdot NH_2$$
$$\underset{CO_3H}{|} + Ca(OH)_2 + CO_2$$
$$= \underset{CO_2-}{\overset{R \cdot CH \cdot NH \cdot CO_2}{|}} \hspace-1em \Big\rangle Ca + H_2O.$$
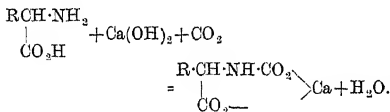
The barium and strontium salts of these complex carbamic acids are much less readily soluble than the corresponding amino-acid, and afford a means of isolating the compounds (D. R. P. 188005, 1906). In order to estimate the amino- acid, the filtrate containing the calcium salt of the carbamic acid is decomposed by heating with boiled-out water into calcium carbonate, and the amino acid; the ratio $CO_2 : N$ is determined by weighing the calcium carbonate thus precipitated, and estimating the nitrogen in the filtrate by Kjeldahl's method (Zeitsch. physiol. Chem. 1908, 54, 423).

dl-Arginine is readily produced by the tryptic fermentation of fibrin, or by heating *d*-arginine nitrate at 210°–220° for 15–20 minutes (Kutscher, Zeitsch. physiol. Chem. 1901, 32, 476) or by heating *d*-arginine in 50 p.c. sulphuric acid in sealed tubes at 160°–180° for

33 hours (Reisser, Zeitsch. physiol. Chem. 1906, 49, 210); it decomposes at 210° (Cathcart, Proc. Physiol. Soc. 1905, 39); the *nitrate* $C_6H_{14}O_2N_4$, HNO_3, has m.p. 216°; the *dinitrate* $C_6H_{14}O_2N_4$, $2HNO_3$, m.p. 151°; the *cupric nitrate derivative* $2C_6H_{14}O_2N_4,Cu(NO_3)_2,3H_2O$, m.p. 228°–229°; the *silver nitrate derivative* $(C_6H_{14}O_2N_4,HNO_3)_2$, $AgNO_3$, m.p. 170°–172°; the *picrate* $C_6H_{14}O_2N_4$, $C_6H_3O_7N_3$, m.p. 200°–201°, is sparingly soluble 100 parts of water at 16° dissolve 0·22 parts; the *picrolonate* $C_6H_{14}O_2N_4,C_{10}H_8O_5N_4$, m.p. 248°, 100 c.c. of water at 16° dissolve 0·03 grams of salt; the *β-naphthalene sulphonate* $C_6H_{12}O_2N_4 \cdot SO_3 \cdot C_{10}H_7, \tfrac{1}{2}H_2O$, has m.p. 85°–90° (Reisser, *l.c.*).

l-Arginine is formed by treating *dl*-arginine carbonate with the expressed juice of calf's liver, the ferment *arginase* present in the extract destroys the *d*-arginine, and does not attack the lævo- isomeride. With the exception of the difference in optical activity, the salts of *l*-arginine are identical with those of the dextro-isomeride, *l-arginine hydrochloride* has $[\alpha]_D^{20°}$ $-20·51°$ (Reisser, *l.c.*).   M. A. W.

ARGININE. This name has also been given to an alkaloid discovered by Quiroga (J. Pharm. Chim. 1896, 16, 293) in a species of laurel (known by the natives as *viraro-mi*), growing in the east of the Argentine and west of Brazil. It forms prismatic crystals, soluble in chloroform or benzene, slightly soluble in ether, petroleum spirit, or water. Its aqueous solutions, acidified with hydrochloric acid, give a white ppt. with bromine water and a white ppt. with alkali soluble in excess. The bark and cambium contain 1·5–1·6 p.c., the wood 0·04–0·05 p.c. of the alkaloid.   H. I.

ARGOL or **ARGAL.** (*Tartre brut*, Fr.; *Weinstein*, Ger.) Crude potassium bitartrate, known as red argol (*Cremore di Vinaccia*), or white argol (*Cremore di St. Artimo*), according to whether it is deposited from the red or the white grape (*v.* TARTARIC ACID).

ARGON. Sym. A or Ar. At. wt. and molec. wt. 39·88. As long ago as 1785, Cavendish (Phil. Trans. 75, 372) made experiments in order to determine whether the inert residue left after withdrawing oxygen, water, and carbon dioxide from air was homogeneous. He sparked a mixture of air and oxygen in presence of potash for the absorption of the acid produced, and removed the excess of oxygen by a solution of liver of sulphur. Only a small bubble of gas remained unabsorbed, and this did not diminish in volume on further sparking with oxygen. Cavendish concluded ' that if there is any part of the ' nitrogen ' of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\tfrac{1}{120}$ part of the whole.'

Cavendish's work was overlooked for more than a century, and attention was only directed to it after the discovery, in 1894, by Lord Rayleigh (Roy. Soc. Proc. 55, 340), that the density of ' atmospheric nitrogen ' was one-half per cent. higher than that of nitrogen prepared by chemical means. This result gave fresh indication of the existence of some hitherto undiscovered gas in the atmosphere, and further

investigations, carried out jointly by Rayleigh and Ramsay (Phil. Trans. 186, 187), led to the isolation of a new gaseous element. The gas, which has a density of approximately 20, and which constitutes nearly 1 p.c. by volume of the atmosphere, was called *argon*, owing to its remarkable chemical inertness, in virtue of which it can be readily separated from the accompanying nitrogen.

Argon occurs in the atmosphere to the extent of 1·3 p.c. by weight (Leduc, Compt. rend. 123, 805) and 0·933 p.c. by volume (Schloesing, Compt. rend. 121, 604; Moissan, Compt. rend. 137, 600). It also occurs in a large number of mineral waters and thermal springs (Bouchard, Compt. rend. 121, 392; Troost and Ouvrard, *ibid.* 121, 798; Moissan, *ibid.* 135, 1278; Moureu, *ibid.* 135, 1335; 142, 1155), and in the volcanic gases of Mt. Pelée (Moissan, Compt. rend. 135, 1085): it is found, moreover, in fire damp and in coal (Schloesing, Compt. rend. 123, 233). Argon has also been observed, together with helium, in the gas evolved on heating numerous minerals.

Preparation. — (i.) *By sparking air with oxygen*, the method originally employed by Cavendish (*v. supra*). The gas is gradually confined over mercury, and a small quantity of potash introduced through a curved pipette. The sparks are passed between the ends of stout platinum wires, fused through the ends of U-shaped glass tubes. These tubes are filled with mercury, and serve to establish electrical connection with the secondary terminals of a Ruhmkorff coil capable of giving a 6-inch spark through air when worked by four lead accumulators. The sparking is usually continued for several hours after contraction has ceased; the excess of oxygen is then absorbed by phosphorus (Rayleigh and Ramsay, *l.c.*; Rayleigh, Chem. Soc. Soc. Trans. 13, 181; Becker, Z. Elek. 9, 600). To save time, it is customary to prepare by method (ii.) a gas consisting mainly of argon, and to employ the method of sparking only to remove the last traces of active gases.

(ii.) *From ' atmospheric nitrogen,' the nitrogen being absorbed by a metal*. In their original investigation, Rayleigh and Ramsay separated argon from nitrogen by continuously circulating the mixture over red-hot magnesium shavings, whereby the nitrogen was absorbed, forming magnesium nitride (*cf.* Ramsay and Travers, Roy. Soc. Proc. 64, 183). This method is no longer used; a dry mixture of pure lime (5 parts) and magnesium dust (3 parts), introduced by Maquenne, is employed instead, which, when heated to redness, produces metallic calcium and absorbs nitrogen with great rapidity. By passing atmospheric nitrogen over this red-hot mixture, and leading the residual gas over metallic calcium heated to dull redness, complete absorption of the nitrogen is readily effected (Moissan and Rigaut, Compt. rend. 137, 773). Metallic lithium has also been employed for the same purpose (Guntz, Compt. rend. 120, 777; 123, 995).

(iii.) The readiest means of preparing argon in quantity consists in leading air slowly over a mixture of calcium carbide (90 p.c.) and calcium chloride (10 p.c.) heated to 800°, the mixture having previously been heated under diminished pressure to drive off any volatile matter. Both oxygen and nitrogen are absorbed by the mixture. The issuing gas is led over hot copper oxide to burn any hydrogen, hydrocarbons, and carbon monoxide present, and the water vapour and carbon dioxide removed. Using 7 kilos. of carbide, 11 litres of argon may be obtained in two days (Fischer and Ringe, Ber. 41, 2017).

The gas prepared by the above methods contains traces of the other inert gases *neon*, *krypton*, and *xenon*, from which it is separated by fractional condensation and evaporation (Ramsay and Travers, Roy. Soc. Proc. 67, 329; Liveing and Dewar, Roy. Soc. Proc. 68, 389). The total quantity of these gases present is, however, only 0·25 p.c., and 85 p.c. of this impurity is neon.

Argon is a colourless gas, condensing to a colourless liquid, boiling at 86·9° abs. (−186·1°), at which temperature its density is 1·4046 (Baly and Donnan, Chem. Soc. Trans. 81, 914). Its m.p. is 83·4° abs. (−189·6°), its critical temperature is 155·6° abs. (−117·4°), and its critical pressure is 52·9 atmos. (Ramsay and Travers, Roy. Soc. Proc. 67, 329).

Argon is more soluble in water than nitrogen, the absorption coefficient being 0·02561, at 1°, and falling regularly to 0·02567 at 50° (Estreicher, Zeitsch. phys. Chem. 31, 176); these figures may, however, be in error by 5 p.c. (*v.* Fox, Chem. News, 99, 250). The refractive index of the gas for sodium light at N.T.P. is 1·0002837 (Burton, Roy. Soc. Proc. 1908, 80, 390); its thermal conductivity is 0·00003894 (Schwaize, Pogg. Ann. 11, (iv.) 303); and its molecular specific heat at constant volume is 2·977 cals. (Pier, Z. Elek. 15, 536). Its coefficient of expansion is 0·003668 (Kuenen and Randall, Roy. Soc. Proc. 59, 60). Argon passes through rubber more quickly than nitrogen (Rayleigh, Phil. Mag. 49, (v.) 220) or carbon dioxide (Kistiakowski, J. Russ. Chem. Soc. 30, 576), and does not pass through heated platinum or palladium; it is diamagnetic (Tanzler, Pogg. Ann. 24, (iv.) 931). (For its rate of effusion, *v.* Donnan (Phil. Mag. 49, (v.) 423).)

The density of argon has been determined by several observers, with the following results: (O=16); 19·940 (Rayleigh, Roy. Soc. Proc. 59, 201), 19·941 (Ramsay, Phil Trans. 186, 238); 19·945 (Fischer and Hahnel, Ber. 43, 1435). Argon is a member of the group of inert gases, and up to the present all attempts to combine it with other elements have failed (Rayleigh and Ramsay, *l.c.*; but *cf.* Cooke, Zeitsch. physikal. Chem. 55, 537).

Atomic and molecular weight. The molecular weight, 39·88, follows from the density determinations just cited; but the atomic weight cannot be determined in the usual manner, since argon forms no compounds with other elements. The ratio of the specific heat at constant pressure to the specific heat at constant volume is 1·644 (Rayleigh and Ramsay, *l.c.*), and this result, from analogy with the case of mercury vapour and by comparison with the ratio 1·666 theoretically required for a monatomic gas according to the kinetic theory, is regarded as proof that

argon is monatomic. Its atomic weight is therefore 39·88.

Spectrum. This is extremely characteristic, and has been carefully examined by Crookes (Phil. Trans. 186, 243), Kayser (Chem. News, 72, 99), Eder and Valenta (Monatsh. 16, 893 ; 17, 50), and by Trowbridge and Richards (Phil. Mag. 43, (5) 77). The most prominent lines are two in the red, having wave lengths of 6965·6 and 7056·4, a yellow line (6038·4), two green lines (5610 and 4702), and a violet line (4200).

ARGYRODITE. A sulpho-germaniate of silver, being the mineral in which the element *germanium* was discovered in 1886. It had, however, been mentioned by A. Breithaupt in 1823, under the name *Plusinglanz.* These occurrences in the Himmelsfürst silver-mine at Freiberg, Saxony, show only botryoidal crusts with a minutely crystallised surface. Later, the mineral was found as distinct, though small, cubic crystals in Bolivia, analysis of which proved the formula to be Ag_8GeS_6 (S. L. Penfield, 1893 and 1894). More recently, cubic crystals of larger size (3–5 cm. across) from Colquechaca, Bolivia, have been described and analysed (V. M. Goldschmidt, 1908). At this locality the mineral appears to be not uncommon, and no doubt large quantities of it have been smelted for silver. In external appearance it is not unlike argentite, but is less sectile than this.

In the Bolivian mineral the germanium may be replaced isomorphously by tin, giving the species *canfieldite* Ag_8SnS_6 (Penfield, 1894). Intermediate members of this series, or stanniferous argyrodite, also occur (Prior and Spencer, 1898).   L. J. S.

ARIBINE *v.* VEGETO-ALKALOIDS.

ARICINE *v.* VEGETO-ALKALOIDS.

ARISTOCHIN. Trade name for di-quinine carbonate $CO(O·C_{20}H_{23}N_2O)_2$.

ARISTOL. Dithymol di-iodide used as an iodoform substitute.

ARJUN WAX *v.* WAXES.

ARMENIAN BOLE *v.* PIGMENTS.

ARNATTO *v.* ANNATTO.

ARNICA *v.* RESINS.

ARNICA YELLOW *v.* AZO- COLOURING MATTERS.

ARNOTTO *v.* ANNATTO.

AROMATIC VINEGAR *v.* ACETIC ACID.

ARRACK. (*Arack* and *Rack,* Fr.; *Arrack: Reisbrauntwein,* Ger.) The term 'araq' or 'arak' was applied by the Arabs to distilled spirits generally, but it is now usually restricted to the spirituous liquor obtained by distillation of the fermented juice of the coco-nut palm (toddy or palm wine), or from rice, or from a mixture of both. Arrack is also made from the succulent flowers of the Bassia genus of trees and from other vegetable products, and is manufactured not only in the East, but also in the West Indies.

Where rice is used, it is steeped in water in large vats and agitated cautiously (so as not to damage the grains, which would interfere with the subsequent fermentation) until about half the rice has begun to germinate. The water is then run off from below, and toddy or

molasses or a mixture of these is added to the rice. The whole is allowed to ferment, and the mixture is then distilled.

This method, which is said to produce the best quality of arrack, obtains at Batavia and in Jamaica, but in India arrack is frequently made from toddy alone.

The best qualities of arrack are agreeable to the taste and wholesome, which cannot be said of the commoner kind made from rice alone, in some parts of India and China. This has a somewhat nauseous odour and taste, due to a volatile oil which distils from the rice, and is narcotic and very unwholesome. Its intoxicating effect is frequently increased by the addition of hemp leaves, poppy heads, stramonium juice, &c.

A large amount of revenue is obtained from the manufacture of arrack in Siam and Ceylon, and the latter exports a considerable quantity to the United Kingdom, where it is used as a valuable ingredient in making *punch.*

An imitation arrack is sometimes made by flavouring rum with flowers of benjamin or benzoic acid.   J. C.

ARROPE. Sherry boiled to a syrup, used for colouring other wines.

ARROWROOT. The starch obtained from the rhizomes of *Maranta arundinacea,* grown in the West Indies. The starch prepared from other roots is often known locally as arrowroot; *e.g.* in Queensland, where the tubers of *Canna edulis* supply such a product.

The composition of the roots of true arrowroot grown in Jamaica is :

		Dextrin	Crude	Ether		
Water	Starch and sugar	fibre	extract	Proteïd	Ash
63·4	27·8	2·1	3·9	0·2	1·6	0·9

(Leuscher, Zeit. öffentl. Chem. 1902, 8, 23.)

Commercial arrowroot contains from 83·5 to 86·9 p.c. starch, 11·0 to 15 p.c. water, proteins from 0·4 to 1·4 p.c., with small quantities (*circa* 0·3 p.c.) of ash, cellulose, and fat.

· (For a series of analyses of arrowroots from various sources, *see* Ballard, Jour. Pharm. 1903, 17, [10] 476.)   H. I.

ARSACETIN. The sodium salt of acetyl-*p*-aminophenyl arsenic acid—

                                    ·OH

                                    .ONa

(*v.* ARSENIC, *Organic compounds of*).

ARSENIC. (*Arsenic,* Fr.; *Arsenic, Arsen,* Ger.) *Schwerbenkobalt, Fliegengift, Näupfchenkobalt Arsenicum. Regulus Arsenici.* Symbol, As; at. wt. 74·9.

Occurrence.—Arsenic, in small quantities, is one of the most widely distributed elements; it is found in mineral and other waters, and in coal smoke, in most pyretic minerals, and in a large number of ores.

In England it occurs principally with *tin ore,* and on the Continent in *mispickel.* Arsenic occurs native (usually associated with iron, cobalt, nickel, antimony, and silver) in crystalline rocks and in the older schists, generally in reniform and stalactitic masses, often mammillated ; it also occurs occasionally in rhombohedral crystals. At Zimeoff in Siberia, large

masses are found; it occurs in the silver-mines of Freiberg, Annaberg, Marienberg, and Schneeberg in Saxony; at Joachimsthal in Bohemia, Andreasberg in the Hartz, Kapnik in Transylvania, Orawitza in the Banat, Kongsberg in Norway, St. Marie-aux-Mines in Alsace, in Borneo, and in the United States.

As *arsenide* it occurs combined with iron in two forms $FeAs_2$ and Fe_2As_4; with nickel as *Kupfernickel* NiAs and $NiAs_2$; with cobalt as *tin white cobalt*, $CoAs_2$. With antimony it occurs as *arsenical antimony*, at Przibram in Bohemia; with blende, antimony and spathic iron, at Allemont, at Schladming in Styria and Andreasberg in the Hartz.

Arsenic is generally present in native sulphur. Combined with sulphur it occurs as *realgar* or *ruby sulphur* As_2S_2 in Hungary, Saxony, Switzerland, and China; and as *orpiment* As_2S_3 in Hungary and the Hartz.

With *sulphur* and *iron* it occurs as *mispickel*, *arsenical pyrites*, or *white mundic* FeS_2FeAs_2; with sulphur and cobalt in *cobalt glance* CoS_2CoAs_2; in *nickel glance* NiS_2NiAs_2, and in a number of other ores, being obtained as a secondary product in the roasting of *tin* and *copper ores*, *copper nickel*, *arsenical fahl ores*, *smaltine*, *cobalt* and *nickel glance*, &c.

With *oxygen*, arsenic occurs as *arsenolite* or *arsenite* As_4O_6, usually as a crust on other arsenical minerals, being formed by their decomposition. With *oxygen* and *cobalt*, it forms *cobalt bloom* or *arsenate of cobalt*; it also occurs as arsenates of iron, copper, and lead.

Preparation.—Metallic arsenic is used only to a small extent in commerce. It is usually prepared from native arsenic, arsenical iron, or mispickel, the latter being the only mineral used to any extent in England. The mineral used is heated in earthenware retorts or tubes laid horizontally in a long furnace. Great care is required in manufacturing the retorts; a mixture of 1 part fresh clay and 2 parts bricks or old retorts powdered, is made into the proper form, coated with a mixture of blood, loam, forge-scales and alum to produce the glaze, and burned. They are very strong and heat-resisting, and quite impervious to the vapour of arsenic. A piece of thin iron sheet is rolled and inserted into the mouth of the retort, and an earthen receiver luted on. On distilling, most of the arsenic condenses in the iron as a nearly white, coherent, internally crystalline mass, and is detached on cooling by unrolling the iron. If required, the arsenic is purified by redistillation.

At Altenberg in Silesia, arsenious oxide is heated with charcoal in an earthen crucible covered with an inverted crucible or conical iron cap. This method is more economical and productive than the one above described, but the metal is grey and pulverulent, and always contains arsenious acid.

It may also be prepared by heating the sulphides with charcoal and sodium carbonate or potassium cyanide.

Properties.—Arsenic is a very brittle steel-grey metalline mass of sp.gr. 5·62 to 5·96, of brilliant lustre, crystallising in rhombohedra, isomorphous with metallic antimony. It is a good conductor of electricity, and is odourless and tasteless.

It is volatile at temperatures above 100°, and is rapidly vaporised at a dull-red heat. At the ordinary pressure it volatilises without previous fusion, the vapour being yellow and of a garlic smell, but when heated under pressure it melts at 500° (Landolt). Joubert states that above 200° its vapour is phosphorescent (Compt. rend. 78, 1853).

When the vapour is condensed at a temperature but little below the volatilising point, *i.e.* when condensed in an atmosphere of arsenic, a nearly white compact mass of strongly metallic lustre is produced which scarcely oxidises in the air even when heated to 80°. When it is deposited on a colder surface or in an atmosphere other than arsenic, it forms less dense, dark-grey crystals which readily oxidise in the air even in the cold, and especially on heating.

Ludwig (Arch. Pharm. [2] 97, 23) has obtained arsenic (?) with a perfectly bright surface resembling freshly granulated zinc, and of the low density 5·395, by distilling in a tube with a small quantity of iodine.

When heated in air it absorbs oxygen, burning with a bluish flame and forming arsenious oxide. In pure water it is unaltered, but when exposed to air it forms a grey powder supposed by some to be a suboxide, but probably a mixture of metallic arsenic and arsenious oxide; this powder is sold as ' fly-powder.' When powdered and thrown into chlorine, it ignites, forming the trichloride; with the aid of heat it combines with bromine, iodine, and sulphur. Hydrochloric acid has but little action on arsenic, but it is rapidly dissolved by nitric acid, aqua regia, or by a mixture of hydrochloric acid and potassium chlorate.

When deflagrated with nitre it forms potassium arsenate.

Bettendorf (Annalen, 144, 110) has obtained a specular, amorphous, vitreous arsenic of sp.gr. 4·69–4·716 by subliming arsenic in a stream of hydrogen and condensing it at 210°–220°. At 360° it is converted into the crystalline form with the evolution of considerable heat, and when heated suddenly it hisses and gives off vapour whilst transforming.

Arsenic is a constituent of many alloys; it is used for bronzing brass and for the manufacture of opal glass.

(For the distribution of arsenic in commercial products, *v. Arsenious oxide.*)

Detection. — Arsenical compounds, when heated on charcoal, give off the characteristic garlic odour and white fumes of the oxide, with a white incrustation on the charcoal some distance from the assay. Metallic arsenic, and many arsenical minerals, such as mispickel, when heated in a tube closed at one end, form a blackish, shining metallic ring on the cooler portion of the tube; if heated in a tube open at both ends, the arsenic is oxidised, and condenses in a ring of white octahedral crystals, their shape being plainly visible under a lens. On cutting off the closed end of the tube containing the metallic mirror, and heating, it is also converted into the white ring higher up the tube. The white crystals dissolve in boiling

water, and the solution shows the usual tests for arsenic. Antimony under like circumstances would produce a white ring, which, however, is not crystalline, and is not soluble in water. Oxides of arsenic require to be mixed with charcoal before they produce the black mirror. Sulphides require the addition of alkaline carbonate or potassium cyanide, or they may be heated with baryta alone (Brame).

White arsenic when heated with about 3 parts of sodium acetate, gives the offensive smell of kakodyl.

In solution the reactions of the two series of compounds, the arsenious and the arsenic, differ considerably ; generally speaking, arsenic com-· pounds may be converted into the arsenious form by heating with sulphurous acid or with a sulphite.

Reinsch's test. If a piece of clean metallic copper is immersed in a solution of arsenious acid or an arsenious compound acidulated with pure hydrochloric acid, it is coated with a grey film, which is probably an arsenide of copper. The action proceeds better at the boiling temperature. The acid must first be tested in the same manner to ensure the absence of arsenic, which is always present in the commercial acid. The metal is washed, dried gently and heated in a tube, when the arsenic becomes oxidised and forms a *crystalline ring* on the colder part of the tube. A film due to antimony, as mentioned before, would not produce a crystalline ring.

This method is used in testing for and removing arsenic from hydrochloric acid, and in toxicology ; by it 1 part of arsenic can be detected in 250,000 parts of solution.

It is not so delicate as Marsh's or the electrolytic method.

When hydrogen is generated in a liquid containing an arsenious compound, the arsenic combines with it and passes off as the gaseous hydride ; many very delicate tests are based on this reaction.

(1) *Fleitmann's test.* The solution is mixed with excess of caustic potash, a piece of *pure* zinc, or of magnesium, or aluminium foil inserted, and the solution heated. A piece of filter paper moistened with silver nitrate is held over the mouth of the tube. In presence of arsenic, arseniuretted hydrogen is produced and reduces the silver on the paper forming a greyish or purplish colour. Antimony is not evolved in this test. Fleitmann's test is therefore a ready means of finding arsenic in presence of antimony ; it is not, however, so delicate as Reinsch's, Marsh's, or the electrolytic method.

(2) *Marsh's test.* This or Reinsch's test is usually used in toxicology. The solution is acidulated with pure hydrochloric acid and introduced into an apparatus in which hydrogen is generated by means of pure sulphuric acid and zinc. Arsenic hydride is formed and is passed through a narrow glass tube, which is heated at one spot by a lamp ; the arseniuretted hydrogen as it passes over the heated portion is decomposed with the precipitation of arsenic as a black ring. In testing for very small quantities of arsenic, the action should be continued for about an hour. A blank experiment should always be performed in the same manner to ensure the purity of the zinc and acid. It is essential not only to obtain zinc and acid which are free from traces of arsenic, but also to see that the zinc used is ' sensitive,' and will permit all the arsenic n the solution to be evolved as arseniuretted hydrogen. The presence in the solution of certain metals—notably iron—is liable to retard, or entirely prevent, the evolution of arseniuretted hydrogen. (On the presence of arsenic in glass as a source of error in the detection of arsenic, *v.* W. Fresenius, Zeitsch. anal. Chem. 22, 397 ; Ber. 17, 2938.) Instead of heating the tube, the gas may be ignited at the mouth of the tube, and the flame caused to impinge on a cold surface of porcelain, or preferably of platinum foil. The arsenic film may be distinguished from that produced by antimony as follows :—

(1) The arsenic film is quickly evaporated, while that of antimony only slowly disappears. Helling (Das Microscop in der Toxicologie) recommends that small spots be heated and the vapour received on a slip of glass, when, under the microscope, the octahedral crystals due to arsenic are visible.

(2) The arsenic film quickly dissolves in a solution of sodium hypochlorite ; the antimony film is very slowly soluble.

(3) The antimony film dissolves quickly in yellow ammonium sulphide, leaving an orange-yellow residue on evaporation ; the arsenic film dissolves very slowly.

Magnesium may also be employed in place of zinc, and E. Davy and Al. Jandousch use an amalgam of 1 part sodium in 8 parts mercury, with or without acid.

The presence of nitrates or nitric acid interferes with this test, and the acids used should be dilute.

(For the detection and estimation of arsenic by electrolytical methods, *v. Arsenic* in art. ANALYSIS, ELECTRO-CHEMICAL.)

Estimation.—Arsenic is usually estimated as (1) magnesium pyro-arsenate ; (2) as arsenic sulphide ; (3) as metallic arsenic.

(1) For this method it is necessary that the substance should be present as an *arsenic* compound. The conversion from the arsenious to the arsenic condition may be effected by heating with nitric acid (*v.* Estimation as sulphide) or hydrochloric acid and potassium chlorate.

The acid solution, which should occupy only a small bulk, is mixed with ' magnesia mixture ' and rendered *strongly* alkaline with ammonia. After standing for 24 hours, the solution is filtered, the last portions of the precipitate, which consists of ammonium magnesium arsenate, being washed entirely on to the filter paper with a little of the filtrate (the volume of this filtrate should be noted roughly). The precipitate is then washed with a mixture of 1 part strong ammonia and 3 parts water, until only a slight opalescence is produced on the addition of nitric acid and silver nitrate to a few drops of the washings. It is then dried, detached as much as possible from the filter paper, and transferred to a weighed porcelain crucible, moistened with nitric acid, dried, and ignited, at first gently, and finally to bright redness. The

paper is moistened with nitric acid, dried, and ignited on the lid, and the crucible and its contents weighed. The ignited residue consists of magnesium pyro-arsenate $Mg_2As_2O_7$, and contains 48·27 p.c. of arsenic.

On account of the solubility of the ammonium magnesium arsenate, an addition should be made to the weight obtained of 0·001 gram for each 16 c.c. of filtrate obtained, not counting the washings.

(2) The arsenic for this method should be in the arsenious form. If *arsenic* compounds are present, they are preferably reduced by passing a current of sulphurous acid through the liquid, the excess of that gas being driven off by subsequent heating. Sulphuretted hydrogen is then passed through the liquid until thoroughly saturated, the liquid left to stand for some time, the excess of sulphuretted hydrogen driven off by heating, and the precipitated arsenious sulphide containing sulphur filtered off. The sulphide is dissolved in ammonia, filtered if necessary, and the arsenic estimated in the solution by one of the three following methods :—

(*a*) The solution is evaporated to dryness in a porcelain dish, then covered with an inverted funnel, and fuming nitric acid added. After the first violent action has ceased, the liquid is heated on a water-bath until the whole of the sulphur has disappeared, and only a small bulk of liquid remains ; ' magnesia mixture ' is then added, followed by excess of ammonia, and the process followed as already described.

(*b*) The ammoniacal solution is evaporated to dryness in a porcelain dish, and heated on a sand-bath to drive off the whole of the free sulphur and carbonise any organic matter (which is frequently present in toxicological analysis) without volatilising any of the arsenious sulphide. The residue is again dissolved in ammonia, filtered if necessary, evaporated to dryness, and gently heated in a weighed porcelain dish, and weighed as arsenious sulphide As_2S_3 (Mohr, Chem. Toxicologie, 56).

(*c*) The arsenic in the solution may be estimated by means of standard iodine solution (Champion and Pellet, Bull. Soc. chim. [2] 26, 541).

(3) For this method the arsenical mirror obtained by the Marsh-Berzelius method or the electrolytic method may be estimated by comparison with standard mirrors obtained under similar conditions to the estimation. Experience has shown that when in the preparation of standard mirrors, the quantities of arsenic used differ by amounts such as 0·002 milligram, a series of mirrors can be obtained showing differences in intensity which are sufficiently distinct and constant to be utilised for comparison.

Separation from other metals.—Certain heavy metals, if present, would be precipitated with the arsenious sulphide by means of sulphuretted hydrogen. From the sulphides of lead, bismuth, &c., the arsenious sulphide can be dissolved by digestion in ammonium sulphide. The solution would also contain antimony and tin, if present. The separation of arsenic from these two metals may be performed as follows :—

From antimony. The mixed sulphides are oxidised with *aqua regia*, as already described, and tartaric acid solution added, followed by excess of ammonium chloride and ammonia.

The latter should produce no opalescence. If a precipitate is produced, a further quantity of tartaric acid or ammonium chloride must be added. The solution is then precipitated by ' magnesia mixture,' and the estimation made as before described.

From tin. A solution of oxalic acid is added to the solution in the proportion of 20 grams of oxalic acid for each gram of tin supposed to be present. The solution should be sufficiently strong for the acid to crystallise out on cooling. The liquid is heated to boiling and sulphuretted hydrogen passed through for 20 minutes, The liquid is allowed to stand for about 30 minutes, and the arsenious sulphide filtered off. It is quite free from tin.

Arsenious chloride in small quantities may be separated from other metals by distillation of the hydrochloric solution (Thorpe, Chem. Soc. Trans. 83, 971) ; in certain metals and alloys by distillation of the finely divided material with a suitable solution of ferric and calcium chlorides, acidified with hydrochloric acid (the materials used should be tested for arsenic). With a solution of zinc and cupric chlorides in hydrochloric acid boiling at 108° both arsenic and antimony may be separated from other metals ; the arsenic is in the distillate from 108° to 115°, the antimony in the distillate from 115° to 160° (Gibb, J. Soc. Chem. Ind. xx. 3).

For the estimation of arsenic in ores, Parnell recommends the following method :—A weighed quantity of the *finely powdered* ore is heated to about 200° in a slow current of chlorine gas, the volatilised arsenious chloride being absorbed in a solution of chlorine water. After evaporation of the excess of chlorine, the arsenic may be estimated by any ordinary method. Antimony, if present in the ore, would also volatilise with the arsenic.

For technical purposes the following methods are largely used :—

A weighed portion is partially decomposed with a minimum quantity of strong nitric acid, dried and fused with sodium peroxide or a mixture of sodium carbonate and nitre. The fused mass is extracted with water and filtered. The solution of alkaline arsenate is acidified with nitric acid and boiled to effect decomposition of either peroxide or nitrite ; it is next carefully neutralised and then acidified with acetic acid, and the arsenic determined by titration with a standard solution of uranium acetate. Pearce recommends separation as silver arsenate from the aqueous extract after fusion ; the silver salt is dissolved in dilute nitric acid and estimated by Volhard's method. With very poor ores to the solution in nitric acid a sufficient quantity of tartaric acid is added, and the arsenic separated as magnesium ammonium arsenate. For the estimation of arsenic in organic salts ignite with sodium peroxide, reduce with hydriodic acid and titrate with iodine and starch in presence of disodium hydrogen phosphate (Morgan, Chem. Soc. Trans. 1909, 95, 1477).

Alloys of arsenic.

Arsenic combines with most metals, in many cases in atomic proportions, the alloys being then known as arsenides. Many natural arsenides occur as minerals.

The alloys may be prepared (1) by fusing the metals under a layer of borax, or in an

atmosphere of some inert gas ; (2) by reducing the arsenite or arsenate of the metal with potassium cyanide ; and (3) in some cases—as with gold, silver, and copper—by placing arsenic in a solution of a metallic salt. W. Spring (Ber. 16, 324) has obtained crystalline alloys of arsenic with other metals by repeatedly compressing a mixture of the constituents at 6500 atmospheres.

When heated out of contact with air, arsenical alloys usually lose a portion of their arsenic ; heated in air the arsenic is oxidised, a portion volatilising, and the remainder forming an arsenite or arsenate of the metal. When heated with nitre, arsenates are produced. (For a list of alloys of arsenic in atomic proportions, probably existing as arsenides, v. A. Descamps, Compt. rend. 686, 1022 and 1065.) Some ancient copper spear-heads from Cyprus contained 1·348 p.c. arsenic, and a bronze figure of the Ptolemaic period from Egypt contained 1·479 p.c.

The presence of arsenic generally renders an alloy more brittle, more fusible, and brighter. In Pattinson's process it tends to render the crystals smaller, and thus lengthens the time required for draining. Its alloys with iron, zinc, and tin are brittle ; with gold and silver, brittle, and grey ; and with lead and antimony, hard, brittle, and fusible. The addition of from 3 to 6 parts arsenic to 1000 lead (with occasionally a little copper) causes the small shot in falling down the tower to form spheres, instead of elongating, as they have otherwise a tendency to do. The arsenic is frequently added in the proper proportions in the form of an alloy of lead and arsenic known as ' temper ' ; this is prepared by fusing together arsenious oxide and lead. By heating a mixture of lead and arsenic to whiteness, Berthier obtained an alloy of the formula Pb_4As, any excess of arsenic beyond that corresponding to this formula being volatilised at that temperature. With copper it forms white, malleable, dense, and fusible alloys. White copper contains about 10 p.c. arsenic. Arsenic is also used in speculum metal, and

FIG. 1.

is frequently present in common Britannia metal.

With potassium and sodium arsenic forms alloys which evolve arseniuretted hydrogen when placed in water. With platinum it forms a fusible alloy, and was formerly used to facilitate the working of that metal.

Arsenic trihydride. *Arsenetted or arseniuretted hydrogen. Arsine.* AsH_3. This gas is formed whenever hydrogen is liberated in a solution containing arsenious acid or an arsenite. as when zinc is introduced into an acid solution of the substance. It is a colourless, neutral, disagreeably smelling gas, slightly soluble in water, and highly poisonous, even when much diluted. At a red heat it decomposes into arsenic and hydrogen.

It is evolved in the bronzing of brass with arsenic, in tinning sheet iron and frequently in the desilverisation of lead with zinc and subsequent heating of the argentiferous zinc with acid. 'It is also occasionally present in the air of rooms of which the wall-paper is coloured with arsenical pigments (*v. Schweinfurth green*). It is a very powerful reducing agent, precipitating silver, gold, and other metals from their solutions. Methods for the quantitative estimation of arsenic are based on this property.

A solid hydride of arsenic appears to exist.

Arsenious oxide. *Arsenious acid. White arsenic. Flowers of arsenic ; commonly known as ' arsenic.'* As_4O_6.

Preparation.—In Cornwall, Devon, and at Swansea, arsenious oxide is principally prepared by roasting mispickel, which occurs mixed with iron and copper pyrites, tin ore, wolfram, blende, galena, &c. These ores, if present in sufficient quantity, are separated as far as possible before roasting ; tinstone by washing the finely powdered ore, and the other minerals by hand. Arsenious oxide is also largely prepared by roasting arsenical silver at Andreasberg, and from arsenical ores of nickel and cobalt.

In ores from which arsenic is produced as a principal product, the arsenical pyrites generally occur to the amount of about 12 p.c.

The ores are usually roasted in a reverberatory furnace. In a common form, the furnace bed is flat, 12–15 feet long and 7–9 feet wide in the middle ; the arch is about 2 feet above the bed, and sinks gradually towards the flue, at which end there is an iron door, through which the ore is raked (Fig. 1).

From 8–15 cwt. of the stamped dried ore is introduced through a hopper over the centre of the fire-bridge and spread over the furnace bed. The heat is raised to dull redness and the ore is frequently stirred to ensure thorough oxidation of the arsenic and sulphur. In about 10 hours these have been expelled as oxides, and the arsenious oxide together with some of the sulphur collects in the flues. The spent ore is removed through an aperture in the bed, which is closed with an iron door during calcination.

Two such furnaces are sometimes built side by side, separated by a wall, and with their flues uniting. The furnace beds slope gently towards a narrow fireplace. In the first instance the ore is introduced through a number of doors on each side of the furnace. As the ore is worked downwards its place is constantly supplied by fresh ore through an opening in the roof.

Brunton's Calciner is much used in Cornwall.
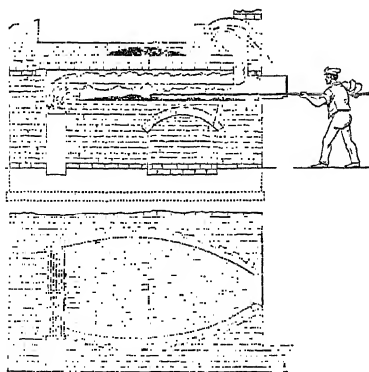
It is practically a reverberatory furnace with a revolving bed. The bed is of firebrick resting on a cast-iron table, and is higher at the centre than at the periphery. It is usually 8 or 10 feet in diameter; it revolves three or four times in an hour by steam or water power, about half-horse power being required. There are two furnaces on opposite sides of the bed.

The dried and finely stamped ore is introduced through a hopper over the centre of the bed. Above the bed are fixed radially three cast-iron frames in which are fastened a number of equidistant iron scrapers shaped like the coulter of a plough and placed obliquely, so that, as the bed revolves, they turn the ore over and outwards towards the periphery of the bed. It is thus thoroughly roasted, and, on reaching the edge, falls into the chamber beneath.

Oxland and Hocking's Patent Calciner (English Pat. 1868, 2950) is largely used, especially for 'rank' ores (Figs. 2 and 3). It consists of a wrought-iron cylinder, which, if 32 feet in length, is lined with sufficient firebrick to leave 4 feet clear internal diameter. Four longitudinal ribs of firebrick occur within the furnace, leaving sufficient space at the upper end for the continuous supply of the ore. The cylinder is generally mounted in an inclined position, the slope being usually $\frac{1}{2}$ to 1 inch per foot, and is turned by means of a turbine or water-wheel once in 8 or 10 minutes upon friction-wheels.

The dried, finely powdered ore is introduced through an archimedean screw, or from a hopper at the upper end, and in the revolution of the tube becomes lifted to a certain height by the ribs of firebrick, and falls in a fine stream through the hot blast. In a few revolutions the ore is completely oxidised, the arsenic burning off first, and finally reaches the lower end of the tube, where it falls through a chamber beneath. A calciner of the above size will roast 6 to 7 tons of ore in 24 hours. In this furnace the amount of air required is minimised, thus rendering the condensation less difficult. The amount of fuel used is also small (*v.* further, Henderson, Proc. Roy. Inst. Mech. Engineers, 1873).

A modification of this furnace was patented by R. & C. Oxland (Eng. Pat. 7285, 1885). It is so arranged that the products pass into the condensing chambers unmixed with other gases. At the lower end of the rotating tube is a cast-iron prolongation, heated externally by a grate and a system of flues surrounding it. At the end of the prolongation is a door for removing the calcined products and a regulator for admitting the required amount of air.

Roasting in muffle furnaces.—This process is used at Altenberg (Figs. 4, 5, and 6) and at Reichenstein in Silesia (Figs. 7 and 8), where wood is cheap.

The ore, reduced to a moderate size and known as *schleich*, is introduced through an opening in the top in charges of about 10 cwt. and spread 2 or 3 inches thick on the floor of the muffle. It is first heated to redness, and then more gently, with the muffle door open, to oxidise the mass thoroughly before sublimation. The operation is completed in 11 or 12 hours.

Condensation of the oxide.—The vapours passing off in the roasting are carried through chambers so arranged that the gases come in contact with a very large condensing surface

passing through a series of chambers before escaping into the air. At the Devon Great
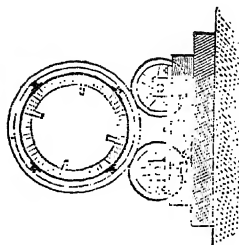
Fig. 3.
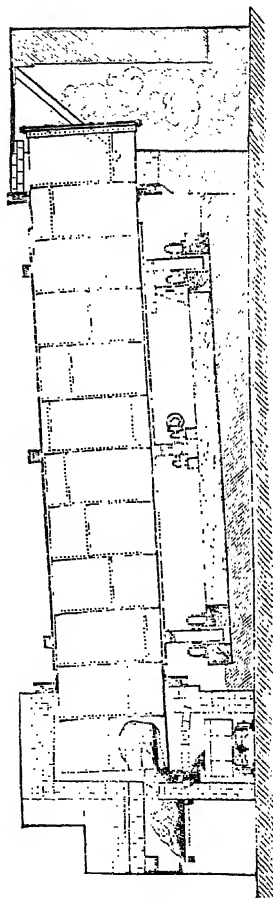
Fig. 2.

Consols and other large works, the chambers are made of thin brickwork covered with iron plates to assist the cooling of the gaseous oxide.

The ores, before calcination, are dried over iron plates or the condensers.

These chambers are cleared at intervals,
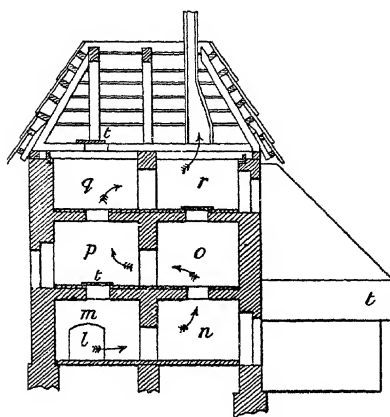
FIG. 4.—VERTICAL SECTION OF POISON TOWER.'

some every fortnight, those at Silesia once in two months. Two sets of chambers are frequently used, so that one set may be working while the other is being cleared.
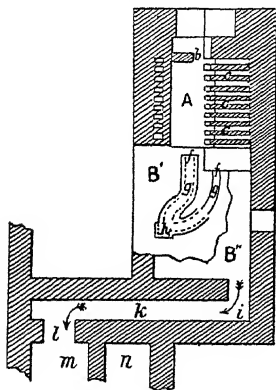
FIG. 5.—GROUND PLAN OF FURNACE.

The oxide produced by all processes except that of the muffle is known as 'arsenical soot,' and is impure, containing carbon and sulphur
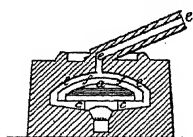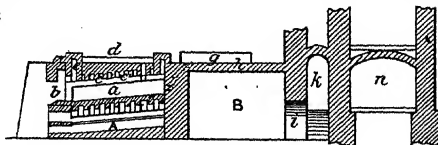
compounds; when so mixed it is of a dark-grey colour and requires to be resublimed.

The condensing chambers connected with the muffles in Silesia are in a lofty building called the 'poison tower' (*Giftthürme*). The gases traverse, by a sinuous course, a series of chambers, depositing the finest product in the lower ones, that in the upper chambers containing sulphur. The chambers are cleared about every 2 months, and contain about 25 tons of white arsenic ('poison flour,' or *Giftmehl*). Being comparatively pure, it does not usually require refining, but may be at once converted into arsenical glass. The workmen engaged in clearing the chambers are clothed in leathern garments with glazed apertures for the eyes, and wear wet cloths over their mouths and noses to absorb the irritating fumes. It is stated at Salzburg that only 'arsenic-eaters' can perform this work continuously.

Refining or resublimation.—For this purpose a reverberatory furnace is used, which is usually much shorter than that in which the calcination is performed. The arsenical soot is charged from the top and paddled down through doors at the side, more being added as it sublimes. The fuel used is smokeless, usually a mixture of anthracite and coke.

The sublimate is collected in chambers similar to those already described. It is white, glistening, and minutely crystalline. It is ground between millstones, and is thence fed into kegs from a hopper through a leathern hose which fastens to the top of the cask and prevents any escape of the powder.

Arsenic glass, or vitreous white arsenic, is prepared by volatilisation of the powder under slight pressure. For this purpose, at Swansea, a cast-iron pan is used 2 feet in diameter and surmounted by a bell 2 feet 6 inches high. The pan is heated to a cherry red, and about $\frac{1}{4}$ cwt. of refined white arsenic introduced through an opening in the top of the bell, which is then closed with a plug. In about 2 hours the whole has evaporated and condensed on the bell as a transparent glass; more white arsenic is then introduced and condensed, until after 24 hours the glass has reached a thickness of about 1 inch. The later charges, owing to the condensing surface being hotter, require about twice as long to condense as the first.

At Silesia the subliming pots are deeper and of greater capacity; they are surmounted by iron drums and conical caps, which condense the 'glass' and open into condensing chambers. The temperature is carefully regulated. The arsenic glass produced amounts to about 92 p.c. of the 'flowers' used.

Analyses of Arsenic Powder and Arsenic Glass.

(1) Powder from Altenberg, from the condenser of a tin roasting furnace, near the furnace end (Lampadius).

(2) Do. from further end of condenser (Lampadius).

(3) Do. from Oberschlema (Lampadius).

Transverse Section.　　　　Longitudinal Section.

FIG. 6.—SUBLIMING FURNACE.

(4) Arsenic glass from Andreasberg (Streng).

	(1)	(2)	(3)	(4)
Arsenious oxide	90·1	95·85	94·31	98·2
Arsenious sulphide	2·05	0·32	1·03	—
Bismuth .			0·25	—
Sulphur . .	0·73	0·71	0·50	—
Ore-dust .	5·51	2·05	3·05	—
Antimonious oxide			—	1·68

Properties and uses of arsenious oxide.—
White arsenic occurs in the amorphous or glassy
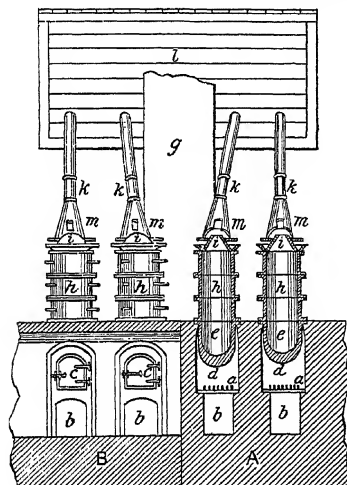
FIG. 7.

form, and in two crystalline modifications:
(1) the octahedral or common form, and (2) in
trimetric prisms, occasionally found in sub-
limates; this form is converted into the octahe-
dral variety when heated or boiled in water.

The amorphous form is transparent when
first prepared, but becomes opaque when exposed
to the air, especially when damp, diminishing
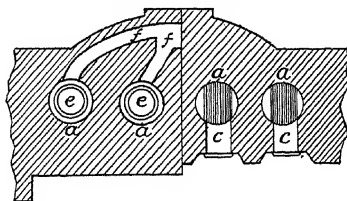
FIG. 8.—REICHENSTEIN FURNACES.

slightly in specific gravity and forming the
crystalline oxide. The action commences at
the outside, so that even after a considerable
time a piece is frequently found with a trans-
parent nucleus. The vitreous form may be kept
in a sealed glass tube unchanged for years.

The vitreous form, according to Buchner, is
soluble in 108 parts of cold water, whilst the
opaque form requires 355 parts; the solubility

of an ordinary piece is therefore doubtful, depend-
ing on the amount of change it has undergone.
It is very soluble in glycerol, and is stated by
Jackson to form *glyceryl arsenite* (Chem. News,
49, 258).

On making a strong solution of the *vitreous*
form in dilute hydrochloric acid by dissolving
3 parts in a mixture of 12 hydrochloric acid
and 4 water, and slowly cooling, it is deposited
in the octahedral form, each crystal as it falls
producing a flash of light (H. Rose). If these
crystals be redissolved or if the opaque form
be used, no light is produced on crystallising,
that phenomenon appearing to depend on the
change of the amorphous into the crystalline
form at the moment of crystallisation.

At about 193° arsenious oxide softens and
sublimes without fusion; it fuses under pres-
sure; its vapour is colourless and odourless.
It is acid to test papers, but does not appear to
form true arsenious acid on solution in water.

Arsenious oxide is a powerful febrifuge, being
sometimes efficacious when quinine has failed.
It is highly poisonous, 2 or 3 grains being a
very dangerous dose. When used habitually,
however, comparatively large quantities may be
taken with impunity. The inhabitants of Styria
eat it under the name of 'hydrach,' to increase
their endurance. Many authentic cases are
recorded of 6 grains and upwards being taken
without ill effect. Arsenic-eaters are stated to
be fresh complexioned, with a tendency to
stoutness, to be long-lived, but to die suddenly.
The workmen engaged in the manufacture of
dyes where arsenic acid is used have been ob-
served to have this tendency to stoutness (*v.*
Roscoe, Mem. of Lit. Phil. Soc. Manchester,
1860). In cases of death from poisoning, the
greater part of the arsenic appears to be con-
tained in the liver and intestines; of the bones,
those of the pelvis and neighbourhood vertebræ
appear to contain most.

In manufactures, arsenious oxide is used:
in glass-making, to remove the colour produced
by the lower oxides of iron; in enamelling;
in calico-printing; as a constituent of white
fire in pyrotechny; for the prevention of boiler
incrustations (40 parts white arsenic to 9 so-
dium carbonate); in the manufacture of arsenic
acid; and of fly and rat poisons; and in the
manufacture of a large number of pigments,
arsenic being found in green, blue, pink, white,
brown, and other colours. As a preservative
it is thrown into the holds of ships, to prevent
vegetable decomposition; as a wash for walls
in India, to prevent insect ravages; to prevent
smut in wheat; and with sodium carbonate as
a wash for sheep; and in arsenical soap, for
preserving skins.

Arsenious oxide is employed in the fixation of
aniline colours, especially of aniline blue. It is
used principally for preparing steam colours,
either as a solution in glycerol containing 4 lbs.
of the oxide to 1 gallon of glycerol, under the
name 'arsenic and glycerine standard'; or as
sodium arsenite, dissolved in sodium carbonate
or borate.

In medicine it is used as Fowler's solution,
which contains 4 grains of the oxide (in the
form of sodium arsenite) in each ounce of fluid.
In India it has been used as a cure for hydro-
phobia and serpent poisoning. In veterinary

surgery it is largely used as a tonic, to eradicate worms, and for improving the coats of horses.

It occurs, either as an impurity or as an adulterant, in a large number of commercial products. Besides the ordinary commercial compounds in which arsenic is expected to be present, it has been found in caustic soda, potassium chlorate, commercial glucose (Clouët and Ritter), and in wine free from artificial colouring matter (traced to sulphuric acid used in purifying the casks). Dr. Tidy found about 38 p.c. of arsenious oxide in some 'violet powder' which had caused the death of at least two children (Lancet, Aug. 21, 1878).

In the year 1900 occurred a serious epidemic of arsenic-poisoning due to contamination of beer through the use of brewing sugars, glucose, or 'invert' sugar containing arsenic. The arsenic was introduced by the use of highly arsenical sulphuric acid in the production of the sugars. The total number of persons who suffered in consequence of the epidemic was certainly 6000, and probably considerably greater. At least 70 deaths were attributed to the epidemic.

Coal or coke used for malt drying always contains arsenic; with an ordinary malt kiln part of the arsenic volatilises and may deposit on the malt. Various methods have been tried and adopted in which it has been found that access of arsenic to malt may be obviated or diminished (Royal Commission: Arsenical Poisoning, 1903).

(For a statement of the amount of arsenic in the varieties of pyrites, and of its distribution in the preparation of sulphuric acid and alkali, v. H. Smith, Phil. Mag. [4] 44, 370; Chem. News, 26, 176; and C. Hjelt, Dingl. poly. J. 226, 174–181.)

Fresenius finds that the arsenic in many chemical glasses is removed by alkaline, but not by acid liquids; the bearing of this on judicial investigations is important.

The commercial article is frequently adulterated with gypsum, chalk, &c., these may easily be detected by heating a little on a knife, when they will remain after the oxide has volatilised.

Sodium arsenite. *Acid sodium arsenite*

$$Na_2O \cdot 2As_2O_3 \cdot 2H_2O$$
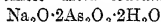
is prepared by dissolving arsenious oxide in a solution of caustic soda or sodium carbonate, and evaporating the solution. The neutral salt, $Na_2O \cdot As_2O_3$, is formed by boiling this compound for some time with sodium carbonate, and washing the residual salt with alcohol (Pasteur).

Potassium arsenite is prepared in a similar manner.

Sodium arsenite is used as a substitute for dung in dyeing, but is not so reliable as the arsenate. It enters anto the composition of all preparations in which arsenious oxide is dissolved with sodium carbonate.

An arsenite of chromium and iron is used as a green pigment in wall-papers.

Scheele's green. *Arsenite of copper. Hydrocupric arsenite.* CuHAsO$_3$.

According to Scheele's method, 11 oz. arsenious oxide are gradually added to a solution of 2 lbs. potassium carbonate in 10 lbs. boiling water; this is filtered and poured into a solution of 2 lbs. copper sulphate in 30 lbs. water, so long as a grass-green precipitate falls. The precipitate is thrown upon a filter cloth, washed with warm water, and dried gently with the production of about 1½ lbs. of the pigment.

Scheele's green is a pulverulent, fine lightgreen colour, formerly largely used in calicoprinting and for wall-papers. It is, however, much less used at the present time. It dissolves entirely in excess of alkali or in acids.

Schweinfurth green. *Imperial green. Emerald green. Mitis green. Aceto-arsenite of copper* (when mixed with gypsum or heavy spar, known also as *Mountain* or *Neuwieder green*).

$$3CuOAs_2O_3 \cdot Cu \cdot (C_2H_3O_2)_2.$$
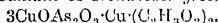
Five parts of verdigris (basic copper acetate) are made into a thin paste with water and added to a boiling solution of rather more than 4 parts arsenious oxide in 50 parts water; the solution is kept boiling during the mixture. If a yellowgreen precipitate falls, a little acetic acid is added, and the solution boiled a few minutes longer; the precipitate becomes crystalline and soon acquires the characteristic green colour.

A very fine product is prepared by the following method:—Boiling, concentrated solutions of arsenious oxide and copper acetate are mixed in such proportions that equal weights of the two substances are present when a bulky olive-green precipitate falls; an equal bulk of cold water is then added and the mixture placed in a flask which it fills to the neck, thus preventing any pellicle which may form on the surface from falling through the liquid and causing a premature crystallisation. The colour under these circumstances takes two or three days to perfect, the beauty of the product being much increased by slow formation. The workmen engaged in the preparation of this pigment do not appear to be injured by it. In contact with organic matter it is, however, liable to change. Bischoff (Zeitsch. anal. Chem. 23, 117) states that microorganisms and fungi act on compounds of arsenic, producing arseniuretted hydrogen; and Fleck, Sonnenschein, and others have conclusively shown that this gas is frequently present in the air of rooms with arsenical wall-paper. By the action of damp and mould on paper coloured with this pigment a peculiar odour is frequently produced, which appears to be due to the formation of diethylarsine (v. ARSENIC MOULD).

Arsenic oxide. *Arsenic acid, Arsenic pentoxide, Acide arsénique, Arsensäure, Acidum arsenicum.* As$_2$O$_5$.

Produced when arsenious oxide is acted upon by an oxidising agent.

On the large scale 4 parts white arsenic are gradually added to 3 parts nitric acid of not less than 1·35 sp.gr. in a vat capable of holding from 65 to 70 kilos. of white arsenic. Great heat is produced and the evolved fumes are passed over coke moistened with water, whereby about two-thirds of the nitric acid is recovered. In 24 hours a syrupy liquid is formed, containing a small quantity of arsenious oxide, which may be oxidised with a little more nitric acid.

Kestner performs the oxidation in large glass flasks, the nitrous fumes being passed through lead pipes and condensed in leaden chambers.

Arsenic oxide has also been prepared by suspending arsenious oxide in water, passing a current of chlorine through the liquid, and evaporating the solution thus produced.

It is a deliquescent solid fusing at a dull-red

heat, of acid metallic taste and acid reaction. It dissolves in 6 parts cold and in 2 parts hot water. A cold, strong solution blisters the skin. Arsenic oxide and its salts are less poisonous than the corresponding arsenious compounds.

Sodium arsenate. *Hydric disodic arsenate*; ' *Dung salt.*' Na_2HAsO_4.

It is prepared by saturating arsenious oxide with crude soda ash, drying, and deflagrating with sodium nitrate in a reverberatory furnace.

Arsenate of soda is largely used in calico-printing as a substitute for dung, its feebly alkaline properties rendering it useful for that purpose.

Arsenate of iron is an amorphous green powder containing 33·6 p.c. arsenic.

Arsenic sulphides. Arsenic forms three well-defined sulphides, As_2S_2, As_2S_3, and As_2S_5, the two former occurring naturally. A large number of other sulphides of indefinite composition also exist.

Realgar. *Disulphide of arsenic. Ruby sulphur. Rothes rauschgelb. Rothes Schwefel. Sulphuré rouge. Orpin rouge. Risigallo. Sandaraca.* As_2S_2.

Prepared by fusing together arsenic and sulphur or orpiment in the proper proportions. On the large scale it is obtained by distilling a mixture of arsenical ores, such as arsenical and iron pyrites, with sulphur or with the sulphide of arsenic precipitated in the purification of sulphuric acid.

The mixture should contain about 15 p.c. arsenic and 26–28 p.c. sulphur; it is placed in flask-shaped earthenware retorts, holding about 60 lbs. when two-thirds full, which are connected with similar receivers. The retorts are gradually heated to redness and kept so for 8–12 hours. The crude realgar should be compact, dark, and rich in arsenic; if sulphur be in excess it is friable and light red. It is re-melted rapidly in cast-iron pans with the requisite amount of sulphur or arsenic, or with realgar of poorer quality. The mass is cleared of slag and heated until quite fluid, and until a small quantity shows the proper appearance on cooling. It is then poured into conical sheet-iron moulds.

Greater care is necessary in the preparation of realgar than of orpiment, and an assay is frequently made to ascertain the exact proportions required before the final melting.

It is hard and brittle, generally opaque, with vitreous conchoidal fracture, orange or hyacinth red in mass and orange-red in powder. Its sp.gr. is 3·4–3·6, and its usual composition is arsenic 75, sulphur 25. It volatilises easily before the blowpipe with a smell of garlic and burning sulphur, is insoluble in water or hydrochloric acid, but soluble in alkaline sulphides.

Realgar is a constituent of blue fire and of ' white Bengal fire,' which is used as a signal light, and consists of realgar 2, sulphur 7, potassium nitrate 24.

The finest variety, especially that which occurs native, is used as a pigment by artists.

Orpiment. *Operment. Gelbes Rauschgelb. Risigallum. Auripigmentum* (of which its usual name is a corruption). *Yellow Sulphide of Arsenic.* As_2S_3.

This sulphide is formed as a yellow precipitate when sulphuretted hydrogen is passed through a solution of arsenious acid in hydrochloric acid.

Schultze (J. pr. Chem. 25, 431) considers that another form of the trisulphide exists which is soluble in water (*v.* COLLOIDS).

On the large scale it is prepared by subliming sulphur with arsenious oxide, 2 parts of arsenious oxide and 1 part sulphur being a common proportion; the colour of the product is lighter when less sulphur is used.

According to R. Wagner, a very fine colour may be produced as follows :—2 parts finely ground barium sulphate are calcined with 1 part powdered charcoal or other carbonaceous matter, and the product is pulverised, mixed with 1 part ground orpiment, boiled in water and filtered. The solution, containing a sulpharsenite of barium, is precipitated by the addition of sulphuric acid. By the addition of a suitable amount of barium chloride before precipitation, the pigment may be correspondingly lightened in colour.

Orpiment is insoluble in water but very soluble in alkaline sulphides. It was formerly much used as a pigment under the name of King's Yellow, but now is largely replaced by chrome yellow. The lighter varieties contain as much as 80 to 90 p.c. of arsenious oxide, and are consequently very poisonous. The darker varieties contain from 1 p.c. to 15 p.c. of the oxide and from 0·2 to 3 p.c. non-volatile matter. It is used in pyrotechny, and the finer kind, especially the mineral, is made into pigment for artists.

It was formerly used as a deoxidising agent in the reduction of indigo blue, and in ammoniacal solution in silk-dyeing. A mixture of 9 orpiment and 1 quicklime made into a paste with water is used under the name of ' Rusma ' for removing hair from skins, but is now generally replaced by the solution of sulphide of lime prepared from the spent lime of gasworks.

Arsenic pentasulphide As_2S_5. Berzelius in 1826 stated that this compound was formed when sulphuretted hydrogen is passed through a moderately concentrated solution of arsenic acid, but the precipitate was generally considered to be a mixture of the trisulphide and sulphur. Bunsen in 1878 showed that it was produced on passing a rapid current of sulphuretted hydrogen through a hot hydrochloric acid solution of an alkaline arsenate, and his results were confirmed by McCay in 1887 (*cf.* Brauner and Tomiček, Chem. Soc. Trans. 1888, 147).

Arsenic pentasulphide is totally insoluble in water, alcohol, or disulphide of carbon. The dry substance, on rubbing in a mortar, becomes strongly electrical.

Arsenic chloride. *Butter of arsenic. Caustic oil of arsenic.* $AsCl_3$ is produced by the action of chlorine on arsenic; by distilling arsenic with mercuric chloride; and by distilling arsenious oxide with strong hydrochloric acid. It is a colourless, oily liquid, of sp.gr. 2·205 0°/4° boiling at 130·2° (Thorpe).

The chloride and iodide are used to a slight extent in medicine. H. W. H.

ORGANIC COMPOUNDS OF ARSENIC.

Cacodyl oxide (*Dimethyl arsine oxide*) $[As(CH_3)_2]_2O$ is formed by the dry distillation of a mixture of equal parts of potassium acetate

and arsenic trioxide. As thus obtained, it is spontaneously inflammable owing to the presence of free cacodyl. When pure, it is an oily liquid, b.p. 150°, insoluble in water, and of a powerful and nauseous odour. It is extremely poisonous. With acids it forms salts, such as *cacodyl chloride* $As(CH_3)_2 \cdot Cl$; this, on heating with metallic zinc, in absence of air, yields *cacodyl* $As_2(CH_3)_4$, as a colourless, liquid, which takes fire on exposure to air. This compound also has an intensely disagreeable smell, and is very poisonous.

Cacodylic acid $(CH_3)_2 \cdot AsO \cdot OH$ is obtained by the oxidation of cacodyl oxide by means of mercuric oxide. It is a crystalline, odourless substance, and is not poisonous (Bunson; Marshall and Greene, Amer. Chem. J. 8, 128). The salts of cacodylic acid, especially the sodium, magnesium. and strychnine salts, have been used in medicine, but have fallen into disfavour on account of their lack of arsenical effect, and of certain unpleasant effects attendant upon their use.

Disodium methylarsenate, 'arrhenal' ('*New cacodyl*') $CH_3 \cdot AsO(ONa)_2$ is prepared by the interaction of methyl iodide and sodium arsenate in the presence of excess of alkali. It is a white crystalline compound, easily soluble in water, but only slightly soluble in alcohol. It may be distinguished from sodium cacodylate by means of mercuric chloride, which gives a reddish-yellow precipitate with arrhenal, but a white precipitate with the cacodylate (Martindale, J. Chem. Soc. Ind. 1907, 907).

The compounds of arsenic with aromatic radicles, especially *atoxyl* and its congeners, have attained importance in the treatment of ' sleeping sickness,' Gambia fever, &c., which are due to the presence of specific trypanosomata in the blood (*v.* Plimmer and Thomson, Proc. Roy. Soc. B. 1907, 505).

Diphenylarsinic acid (*Phenyl cacodylic acid*) $(C_6H_5)_2 \cdot AsO \cdot OH$ is prepared as follows : Diphenyl-arsenious chloride, one of the products of the interaction of mercury diphenyl and arsenious chloride (Michaelis, Ber. 8, 1316 ; 9 1566), is mixed with water and treated with a rapid stream of chlorine at a temperature of 60°–70°.

Diphenylarsinic chloride $(C_6H_5)_2AsCl_2$ is thus formed : the solution is evaporated to dryness on the water-bath, and the residue taken up with water, from which the acid can be crystallised in long needles ; m.p. 174° (Michaelis, Annalen, 201, 231 ; 321, 151). Martindale recommends the use of ether as a solvent. (For an alternative method of preparation, *see* Sachs and Kantorowiez, Ber. 41, 2767.)

p-**Tolylarsinic acid** $CH_3 \cdot C_6H_4 \cdot AsO(OH)_2$ is prepared by passing chlorine into a mixture of 1 part *p*-tolyl-arsenious chloride and 5 parts water at 60°–70°. The solution is evaporated to dryness and the residue boiled with water, from which the acid crystallises (Martindale). The acid has been found efficacious in destroying trypanosomes (Plimmer and Thomson, *ibid.*).

p-**Aminophenylarsinic acid** (*Arsanilic acid*) was first prepared by Béchamp in 1863 (Compt. rend. 56, 1172), by heating aniline arsenate at 190°–200°. He supposed it to be an anilide of arsenic acid. Ehrlich and Bertheim have shown (Ber. 40, 3292) that the acid has the composition

expressed by the formula $NH_2 \cdot C_6H_4 \cdot AsO(OH)_2$. It is weakly basic, and forms salts with acids which are at once hydrolysed by water.

Sodium *p*-aminophenylarsinate, known as '*atoxyl*' (*arsamin, soamin*) $NH_2 \cdot C_6H_4 \cdot AsO(OH)ONa$, is obtained by neutralising the above acid with soda. It is a white salt, crystallising with an amount of water variously stated to be between 2 and 6 molecules, and effloresces on exposure to air (Moore, Nierenstein and Todd, Biochem. Jour. 1907, 300 ; *v.* also Ehrlich and Bertheim). The anhydrous salt is soluble in methyl alcohol, but almost insoluble in ether, acetone, benzol, or chloroform. (For its therapeutic action, *see* Pharm. Chem. Jour. 1907, 528.) It is at present the compound of arsenic most largely used in combating trypanosomes.

Atoxyl solutions should be made with cold, boiled water and kept in the dark. They must not be allowed to become alkaline, and should be boiled for two minutes (not more) before use.

(For a method of estimating either arrhenal or atoxyl, *v.* Bougault, J. Pharm. Chim. 1907, 13.)

Mercury *p*-aminophenylarsinate (*Asyphil*) has been suggested as a substitute for atoxyl. It may, in common with many other insoluble organic compounds of arsenic, be dissolved in glycerol, and this solution, strong or diluted, used for injection. It is said that such a solution has a stronger action on trypanosomes than has atoxyl (P. Wolff, Ger. Pat. 213394, 1908).

Acetyl-*p*-aminophenylarsinic acid (*Acetyl-arsanilic acid*) $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot As(OH)_2$ is prepared by acetylating 31 parts of atoxyl with 55 parts of acetic anhydride, and then adding 300 parts of water and 52 parts hydrochloric acid (Ber. 40, 3292). By neutralising the acid with soda,

Sodium acetyl-*p*-aminophenylarsinate ('*Arsacetin,*' *acetyl-atoxyl*) $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot AsO(OH) \cdot ONa$ is obtained as a white crystalline powder, soluble in water (1 : 10). This compound is stated to be less toxic than atoxyl (*v.* Extra Pharmacopœia, xiii. 168), and its solutions can be sterilised by heat and stored without alteration. It has been successfully exhibited in cases of syphilis, and is very active in combating trypanosomes.

Phenylglycine-*p*-arsinic acid

$$CO_2H \cdot CH_2 \cdot NH \cdot C_6H_4AsO(OH)_2$$

is prepared either by mixing sodium *p*-amino-arsinate (' atoxyl ') and chloroacetic acid in hot water, or by hydrolysing with alkalis the nitrile $CN \cdot CH_2 \cdot NH \cdot C_6H_4AsO(OH)_2$ produced by warming together in aqueous solution, *p*-aminophenyl-arsinic acid, potassium cyanide and 40 p.c. formaldehyde (D. R. P. 204664).

Arsenophenylglycine (' 418 ')

$$As_2(C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H)_2,$$

a reddish-brown powder, soluble in aqueous sodium carbonate, but insoluble in dilute mineral acids, and the ordinary organic media, is prepared by reducing the preceding compound with alkaline sodium hyposulphite (D. R. P. 206057 ; U.S. Pat. 888321). This substance has given promising results in sleeping sickness. Ehrlich supposes that it acts on that part of the trypanosome concerned with multiplication. The sodium salt is a readily soluble yellow powder, which, however, can be preserved only in sealed

tubes ; it has found employment in a 5 p.c. ointment in eye affections and eczema.

p-Hydroxyphenylarsinic acid

$$HO \cdot C_6H_4 \cdot AsO(OH)_2,$$
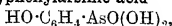
yellow prisms ; m.p. 173°–174°, is obtainable either directly by heating phenol and crystallised arsenic acid at 150° for 4 hours, or by decomposing with hot water the diazonium derivative of *p*-aminophenylarsinic acid.

2-Nitrophenol-*p*-arsinic acid

$$HO \cdot C_6H_3(NO_2) \cdot AsO(OH)_2,$$
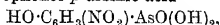
is prepared by dissolving the sodium salt of the preceding acid in cold concentrated sulphuric acid and adding to the solution at 0° the calculated amount of nitric acid (sp.gr. 1·4) mixed with an equal volume of sulphuric acid.

4 : 4′-**Dihydroxy**-3 : 3′-**diaminoarsenobenzene hydrochloride** $As_2[C_6H_3(OH).NH_2]_3,2HCl$ (*Salvarsan*, ' 606 ') is produced by reducing the preceding compound with sodium sulphide, when the free base separates as a yellow crystalline precipitate, soluble in dilute hydrochloric acid or aqueous alkalis, and reprecipitated from the latter by acetic acid. This compound appears to have a specific action on trypanosomes and spirochetes with a minimum evil after-effect on the host of these parasitic organisms. Very remarkable curative results have been obtained in syphilis, relapsing fever, framboesia, and fowl spirillosis. The drug has also been exhibited with some success in malaria and leprosy ; it is applied in the form of injections, which may be either subcutaneous, intramuscular, or intravenous.

When a sufficient dose is administered it is frequently found that complete disappearance of the specific organism is effected after a single injection (*v.* Ehrlich and Hata, Die experimentelle Chemotherapie der Spirillosen (Syphilis, Rückfallfieber, Hühner Spirillose, Framboësie) ; J. Bresler, Die Syphilisbehandlung mit dem Ehrlich-Hata'schen Mittel ; Martindale and Westcott, Salvarsan or '606,' 1911). (For organic arsenic compounds containing two or thre aromatic or hydroaromatic groups, *v.* Chem. Soc. Trans. 1908, 93, 1180, 1893, 2144 ; 1909, 95, 1473 ; Ber. 1908, 41, 931, 1672 ; 1910, 43, 924.)

Arsenogene is an indefinite compound of peptonised casein and arsenic, recommended for medicinal use by Salkowski (Apoth. Zeit. 1908, 114).

The preparation of albuminoid compounds of arsenic has been patented by Klopfer (D. R. P. 214717, 1908) and Gnezda (D. R. P. 201370, 1906).

(For the determination of arsenic in organic compounds, *see* Little, Cahen and Morgan, Trans. Chem. Soc. 1909, 1477.)

ARSENICAL PYRITES or *Arsenical mundic.* Names commonly used by miners for the mineral *mispickel* (*q.v.*) or *arsenopyrite* (FeAsS), which is the principal ore of arsenic.

ARSENIC MOULD. *Penicillium brevicaule.* This organism, first obtained by Gosio, in presence of an arsenic compound, forms *diethylarsine* $AsH(C_2H_5)_2$, to which the poisonous gas developed by wall-papers containing arsenic is probably due. The formation of diethylarsine by the action of this mould has been used as a test for arsenic by Markmann (Chem. Zentr.

1900, ii. 1187) ; Galli-Valerio and Strzyzowski (*ibid.* 1901, i. 63).

Penicillium brevicaule also gives garlic or mercaptan-like odours with compounds of selenium and tellurium (Maassen, Chem. Zentr. 1902, i. 1245).

ARSENOGENE. Trade name for an albuminous preparation of arsenic and iron obtained by heating peptonised casein with arsenic acid and ferric ammonium sulphate. Used in medicine (Salkowski, Apoth. Zeit. 1908, 23, 114).

ARSENOPYRITE *v.* MISPICKEL.

ARSINE. *Arsenic trihydride* (*v.* ARSENIC).

ARTEMISIN. An alkaloid isolated by Merck from the mother liquors obtained in the preparation of santonin from the seeds of *Artemisia maritima.* Forms colourless crystals ; m.p. 200° ; sparingly soluble in water, more soluble in alcohol ; $[\alpha]_D -84.3°$. With hot soda solution gives a carmine red solution, colourless on cooling. Gives an oxime with hydroxylamine, and a hydrazone with phenylhydrazine (Bertolo, Pharm. J. 1902, 489 ; Freund and Mai, Ber, 1901, 3717 ; *cf.* Wedekind and Koch, Ber. 1905, 1845).

ARTICHOKE. Three vegetables are known by this name : (1) the Globe artichoke—the flower head of *Cynara scolynus* ; (2) the Jerusalem artichoke—the tuber of *Helianthus tuberosus* ; (3) the Japanese or Chinese artichoke —called also Chorogi—the tuber of *Stachys tuberifera.*

The following are analyses of the tubers of the two latter :—

	Water	Protein	Fat	Carbo-hydrates	Ash
Jerusalem artichoke	79·5	2·6	0·2	16·7	1·0
Stachys tuberifera	78·05	4·32	0·16	14·63	1·21

(Strohmer and Stift, Bied. Zentr. 21, 820.)

The ' protein' of the Jerusalem artichoke includes much material other than true proteid ; the carbohydrates consist largely of inulin and levulin.

According to Tanret (Compt. rend. 1893, 117, 50), two other carbohydrates—*helianthenin* m.p. 176°, $12C_6H_{10}O_5+3H_2O$, and *synanthrin*, m.p. 170°, $8C_6H_{10}O_5+H_2O$—are also present, and the levulin or synanthrose described by other observers as occurring in artichokes, is a mixture of saccharose and synanthrin.

The tubers of *Stachys tuberifera* contain many nitrogenous substances of an amide nature— *glutamine, tyrosine, arginine, choline, trigonelline,* and the characteristic body, *stachydrine*

$$CH \underset{\substack{|\\ H_2-N(CH_3)_2}}{\overset{CH_2-CH-CO}{\diagup}} \diagdown O$$
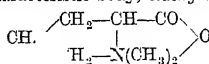
The amount of the last-named is estimated at 0·18 p.c. of the dry substance (Schulze and Trier, Zeitsch. physiol. Chem. 1910, 67, 59). The characteristic carbohydrate is *stachyose* $C_{18}H_{32}O_{16},3H_2O$ (*q.v.*) H. I.

ARTOCARPUS BARK. The inner bark (bast) of the bread-fruit tree [*A. incisa* (Linn.)] is used by the South Sea Islanders for making ropes and clothing. According to Moeller (Dingl. poly. J. 231, 463), this fibre would probably be a very useful one. It can be obtained in large quantities.

ARTOCARPUS INTEGRIFOLIA (Linn. f.). (*Jack Tree*) *v.* JACKWOOD ; DYES, NATURAL.

ARUM MACULATUM (Linn.). The common arum, ' wake robin,' or ' lords and ladies,' ' cows and calves,' formerly known as ' abron ' janus, ' ramp,' ' starch wort,' contains a starch which was made into a kind of arrowroot in the Isle of Portland, and was the active ingredient of ' Portland powder,' a so-called specific for gout. Occasionally sold in Paris as a cosmetic, under the name of *poudre de Cypre*.

Amorphophallus campanulatus (Blume) is used in India as a vegetable and also in medicine, as are other of the Arums. Many of the Aroideæ act as poisons, their toxic action being due apparently to the irritation induced by the raphides contained in the cells (Pedler and Warden, Jour. Asiatic Soc. of Bengal, 57. 2, 106 ; Stahl ; Pflanzen und Schnecken, Zeitsch. Nat. u. Med. Jena, xxii. N. F. xv. 1888).

ASAFŒTIDA *v.* GUM RESINS.

ASAPROL *v.* ABRASTOL.

ASARUM CANADENSE (Linn.). A plant indigenous to North America, where it is known by the names of ' Wild Ginger,' or ' Canada Snake-root.' The rhizome yields on distillation an essential oil used in perfumery, containing a phenol $C_8H_{12}O_2$, *d-* and *l-* pinene, *d*-linalool, *l*-borneol, *l*-terpineol, geraniol, eugenol methyl ether, a lactone $C_{14}H_{20}O_2$, a mixture of fatty acids, including palmitic and acetic, and a blue oil of undetermined composition, consisting of oxygenated substances of alcoholic nature (Power and Seed, Chem. Soc. Trans. 1902, 81, 59).

ASBARG. Asbarg consists of the dried flowers and flowering stems of the *Delphinium zalil*, which is found in great quantity in Afghanistan. The dyestuff is collected and taken to Multan and other Punjab towns, from which it is conveyed all over India. It is much used in silk-dyeing for the production of a sulphuryellow colour known as ' gandkaki,' and,together with *Datisca cannabina*, to obtain a similar shade on alum-mordanted silk ; it is also used in calico-printing. The flowers, which are bitter, are likewise employed medicinally as a febrifuge.

The colouring matters of asbarg are present entirely as glucosides, and are best isolated in the crude condition by digesting the boiling aqueous extract with a little sulphuric acid (Perkin and Pilgrim. Chem. Soc. Trans. 1898, 268). A brownish-yellow powder thus separates, which contains three substances : *isorhamnetin, quercetin*, and *hæmpferol*.

Isorhamnetin $C_{16}H_{12}O_7$, the sparingly soluble constituent, forms yellow needles resembling rhamnetin in appearance. With lead acetate in alcoholic solution, an orange-red precipitate is formed, whilst ferric chloride gives a greenishblack colouration. Fused with alkali, *phloroglucinol* and *protocatechuic acid* are produced, and when air is aspirated through its alkaline solution, *phloroglucinol* and *vanillic acid* are obtained.

With acetic anhydride *iso*rhamnetin gives a *tetra-acetyl*, derivative $C_{16}H_8O_7(C_2H_3O)_4$, colourless needles, m.p. 195°–196° ; and with methyl iodide a *trimethyl ether*, which is identical with *quercetin tetramethyl ether*. As, moreover, by the action of hydriodic acid *iso*rhamnetin yields quercetin, its constitution can only be represented as follows :—
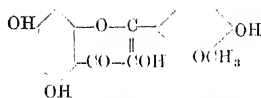
The dyeing properties of *iso*rhamnetin are similar in character to those given by hæmpferol *iso*Rhamnetin is also present in yellow wallflowers (*Cheiranthus cheiri*) (Perkin and Hummel); in red clover flowers, *Trifolium pratense* (Power and Salway, Chem. Soc. Trans. 1910, 97, 245). A description of the more soluble colouring matters quercetin (*quercitron bark*) and hæmpferol (*Delphinium consolida*) are given elsewhere.

In *dyeing properties* asbarg closely resembles quercitron bark, but yields with aluminium mordant, a purer or less orange-yellow. It is, however, a much weaker dyestuff, having but 35 p.c. the dyeing power of quercitron bark. The colouring matter of the flowers, minus the flowering stalks, is present to the extent of 3·47 p.c.　　　　　　　　　　　　A. G. P.

ASBESTOS, from ἄσβεστος, ' unquenched.' Both in ancient and modern times various silicate minerals, closely resembling one another in their finely fibrous texture and flexibility, have been and are still confused under this name. The same is true also of the name ' amianthus ' or ' aminatos ' (ἀμίαντος, ' undefiled,' because not injured by fire). They are, therefore, collective names of no more definite signification than the adjective ' asbestiform.' Mineralogists are, however, agreed in limiting the name asbestos to the fibrous forms of hornblende, but this limitation is not generally observed. Any ambiguity may be avoided by using the terms amphibole-asbestos (or hornblende-asbestos), serpentine-asbestos, &c., for these asbestiform minerals. The finely fibrous texture is, of course, an accidental character of the mineral species, depending on the enormous elongation in one direction of the individual crystals which form the aggregate. Such a character might, indeed, be assumed by many kinds of minerals ; but it is only the following that are of any importance in this connection :—

Tremolite, $CaMg_3(SiO_3)_4$.
Actinolite, $Ca(Mg,Fe)_3(SiO_3)_4$.
Crocidolite, $NaFe'''(SiO_3)_2.Fe''SiO_3$.
Anthophyllite, $(Mg,Fe)SiO_3$.
Serpentine, $H_4Mg_3Si_2O_9$.
Palygorskite group $\{ nH_2Mg_2Si_3O_{12}$
(pilolite, &c.), $\{ mH_2Al_2Si_4O_{12},5H_2O.$

The first two of these differ only in the relative proportions of the mutually replaceable magnesium and ferrous iron (and consequently also in their colours, which are white and green respectively), and they are merely varieties of the species amphibole or hornblende. Crocidolite is another species of the amphibole group of minerals, crystallising in the monoclinic system, and also with an angle of 56° between its prismatic cleavages. It is known in the trade as ' blue asbestos,' and it gives the name to the Asbestos Mountains in South Africa, where it is found. Whilst hornblende is more frequently found as stout crystals and compact masses, crocidolite, on the other hand, is as yet known only in the finely fibrous form. Anthophyllite also belongs to the amphibole group, but is orthorhombic in

crystallisation. Some of the asbestos mined in the United States is of this kind. Serpentine occurs in nature as large rock-masses, and the compact rock is frequently traversed by veins of fibrous material of the same composition; the latter is known to mineralogists as *chrysotile*, and in the trade as ' asbestos ' or ' Canadian asbestos.' In the minerals of the palygorskite group (A. Fersmann, Bull. Acad. Sci. St. Petersburg, 1908, ii. 255, 637) the fibres rarely show a parallel arrangement, but are more usually matted and interwoven, giving felted masses known as ' mountain-leather,' ' mountain-cork,' and ' mountain-wood.' It is, however, to be remembered that these trivial names may also be applied to similar aggregates of fibrous amphibole.

From a practical point of view, the most important of these are *tremolite-asbestos* and *serpentine-asbestos*, which in the trade are known as ' Italian asbestos ' and ' Canadian asbestos ' respectively. The former is met with as aggregates or bundles of white or greyish fibres, sometimes several feet in length, usually arranged parallel to the surfaces of crevices in the metamorphic and crystalline rocks of mountainous districts. It is mined in the Alps, Urals, and Appalachians. The supply is limited and uncertain, and the hardness of the enclosing rocks makes mining difficult. The principal mines are those in the north of Italy, in the Susa and Aosta valleys in Piedmont, and the Valtellina in Lombardy.

Serpentine-asbestos, or chrysotile, occurs in small veins forming an irregular network in serpentine-rock. It has in the closely compacted mass an oil-yellow or greenish colour with a pronounced silky lustre and a certain degree of translucency. When rubbed or crushed, it readily separates into white cottony fibres (pierre à coton of the French-Canadians). The fibres are arranged perpendicularly to the walls of the vein, and are usually only an inch or two in length, never exceeding 6 inches. The mineral usually contains 2–3 p.c. FeO isomorphously replacing magnesia. Although chrysolite is found at all the localities where serpentine-rock occurs (*e.g.* the Lizard district in Cornwall), it is only in Canada that it is mined to any large extent, and there only since 1878. The mining districts are near the villages of Thetford, Black Lake, East Broughton, and Danville in Quebec. The asbestos quarried by the ancients at Karystos, in Eubœa (Karystian stone), and in Cyprus, was also a serpentine-asbestos (J. W. Evans, Mineral. Mag., 1906, xiv. 143). It was used for wicks in the perpetually burning lamps of the temples; and was woven into napkins, which could be cleansed by fire, and into cremation shrouds.

These two kinds of asbestos—the hornblende-asbestos and the serpentine-asbestos—differ somewhat in their resistance to acids and heat. Chrysotile is decomposed by hydrochloric and sulphuric acids; at a red heat (but not below) it loses water, and the fibres can be fused in the bunsen-flame. Tremolite-asbestos is not attacked by acids, and it is more difficultly fusible. (Crocidolite fuses readily to a black, magnetic glass.) On the other hand, the fibres of chrysotile are more flexible and more suitable for textile purposes. Notwithstanding these

differences, the two varieties are put to the same uses, but serpentine asbestos is employed in far larger quantities. Spun asbestos is largely used for steam packings, fireproof curtains; and as cloth, twine, and rope it finds a variety of applications. As an insulating material, asbestos fibre is used for coating steam and hot-water pipes and cold-storage plants; and as a lining in safes, stoves, and furnaces. For use as a constructional fireproof material, it is made into bricks, boards, millboards, plasters, and paints, being often mixed with other materials, The so-called ' asbestic,' largely used for wall plaster, is prepared by grinding the poorer material and waste, which consists of narrow veins of asbestos still enclosed in the serpentine-rock. In the laboratory, asbestos is used for filtering (a pure white tremolite-asbestos being best for this purpose), for stoppings in combustion tubes, and in the form of card for supports. Asbestos paper or twine, soaked in sodium silicate and afterwards treated with calcium chloride solution, can be used for repairing glass apparatus.

The production of Canadian asbestos in 1908 amounted to 65,534 short tons (of 2000 lbs.), valued at about 510,000*l.*; and, in addition, 25,239 tons of ' asbestic,' valued at about 5000*l.* The prices per short ton vary from $150 to $350 (about 30*l.*–70*l.*) for the better qualities (' crude'), descending to $10 for the smaller material (' fibre ' and ' paper stock ').

References.—F. Cirkel, Asbestos, its Occurrence, Exploitation, and Uses (Mines Branch, Ottawa, 1905); R. H. Jones, Asbestos (London, 1890), and Asbestos and Asbestic (London, 1897); G. P. Merrill, Asbestos and other Asbestiform Minerals (Proc. U. S. Nat. Museum, 1895, xviii. 281), and ' Non-metallic Minerals ' (New York, 1910); Production and Uses of Asbestos (Bull. Imp. Inst. 1905, iii, 277); The Technical Preparation of Asbestos, (*ibid.* 1908, vi. 393); J. S. Diller, Mineral Resources of the United States, for 1908, 1909, ii, 697; H. F. Olds, Blue Asbestos [Crocidolite in South Africa] (Trans. Inst. Mining and Metall. 1899, vii. 122). L. J. S.

ASDUANA *v.* BRIDELIA BARK.

ASEPTIN. Trade name for a mixture of hydrogen peroxide, boric acid, and salicylic acid, used as an antiseptic.

ASEPTOL. Trade name originally given to a solution of *o*-phenolsulphonic acid $C_6H_4(OH)SO_3H$. It is a thick reddish fluid, of 1·45 sp.gr., having a faint odour like phenol, occasionally called *sozolic acid*. It is an antiseptic, but does not possess the poisonous action peculiar to phenol, and is therefore recommended for surgical and ophthalmic operations (Chem. Zentr. 1884, 720).

The aseptol of Merck is *p*-phenol sulphonic acid mixed with about 6 p.c. of the *o*-acid (Obermiller, Chem. Zentr. 1907, 1615).

The name is also given to a preparation containing from 0·25 to 10 parts potassium oxyquinoline sulphate, 0·5 to 10 parts soap, dissolved in 1000 parts of water, mixed with terpineol or other aromatic substances, and occasionally glycerol (Pharm. Zeit. 1897, 770).

Aseptol is also the name given to an ill-defined mixture of phenyl ethers and sulphonated phenols, obtained by the action of sulphuric

acid on phenol in presence of alcohol (Trillat, J. Soc. Chem. Ind. 1892, 1028).

ASFRAX or *Trayamana.* An Indian drug, consisting of the flowers, flower-stalks, and immature fruit of a species of *Delphinium.* Used in Bombay as a medicine, and as a yellow dye for silk (Dymock, Pharm. J. [3] 8, 161).

ASH. This term is sometimes used to denote the inorganic or mineral matter contained in any substance, but more generally refers to the residue left on completely burning or incinerating it. The two meanings are not necessarily the same, since in any animal or vegetable substance the inorganic constituents are usually present in very different states of combination to those in which they occur in the residue left when the substance is completely oxidised.

To ascertain the exact amount and composition of the inorganic matter present in any organic substance is often a matter of considerable difficulty, and, in many cases, is impracticable.

The term 'ash' should be used, therefore, only in the second sense given above.

Most animal and vegetable substances leave, on combustion, a residue containing the following constituents in varying proportions :—

Acidic	Basic
Chlorine	Sodium
Carbon dioxide	Potassium
Sulphur trioxide	Calcium
Sulphur	Magnesium
Phosphorus pentoxide	Iron
Silica	Manganese

Other constituents, generally in small quantities, are also often present.

In the original substance the greater portions of the basic constituents in the above list are probably present in combination with organic acids, and, consequently, are left in the ash as carbonates (often largely the case with potash and soda) or as oxides (*e.g.* portions of the lime, magnesia, oxides of iron, and manganese) ; while the carbonates, sulphates, and phosphates are, in many cases, derived from organic combinations of carbon, sulphur, and phosphorus existing in the original substance. The determination of the amount and composition of the ash of animal and vegetable substances, though, perhaps, inadequate to ascertain the exact nature of the inorganic constituents of the organised bodies, affords valuable information as to their fitness as foodstuffs, and as to the needs of animals or plants.

In the process of incineration, there is great danger of loss of chlorides of potassium and sodium by volatilisation, also of reduction of phosphates and sulphates by the reducing action of the hot carbon. Berthelot proposed to overcome these difficulties by heating in a current of oxygen, the substance to be incinerated being previously mixed with a known weight of sodium carbonate (Compt. rend. 128, 23).

Shuttleworth (Chem. Zentr. 1899, ii. 144) has suggested the addition of calcium acetate in order to prevent the sintering which is so often an obstacle to complete incineration, and has devised a special platinum vessel in order to prevent loss of chlorides by volatilisation, and to hasten incineration. A modified form of this apparatus is described by Tucker (Ber. 32, 2583).

A convenient method of minimising the loss of chlorides by volatilisation is to char the substance thoroughly at a moderate temperature, then cool and extract the black residue with water, filter off the soluble matter, and complete the incineration of the residue after drying. When all black particles have disappeared, the residue is allowed to cool, the aqueous extract added, evaporated to dryness, and then moderately heated. Addition of ammonium nitrate to the black char hastens the combustion of the carbon.

Ash of animals. The proportion of ash constituents present in the whole body of an animal depends largely upon its condition, being greater in lean than in fat animals. According to the Rothamsted experiments, the following table gives the average proportions of ash and of its main constituents in the whole bodies of various farm animals in a fatted condition :—

	Total ash	Phosphoric acid P_2O_5	Lime CaO	Magnesia MgO	Potash K_2O
Fat calf	3·9	1·54	1·65	0·08	0·21
Half-fat ox	5·1	1·84	2·11	0·09	0·21
Fat ox .	4·2	1·55	1·79	0·06	0·18
Fat lamb	3·2	1·13	1·28	0·05	0·17
Store sheep	3·3	1·19	1·32	0·06	0·17
Fat sheep	3·0	1·04	1·18	0·05	0·15
Store pig	2·8	1·07	1·08	0·05	0·20
Fat pig	1·7	0·65	0·64	0·03	0·14

The other constituents of the ash consist chiefly of sodium, chlorine, fluorine, iron, manganese, iodine, and silica.

The bones and teeth contain the greater part of the phosphoric acid, lime, magnesia, and fluorine ; potash is present largely in muscle, blood, and many of the secretions ; sodium, chlorine and iron are largely present in the blood and the secretions, while iodine is mainly accumulated in the thyroid gland.

(For the amount and composition of the ash of various portions of the animal body, and of certain animal products, *v.* BONES ; BLOOD ; MILK ; &c.)

A characteristic of the ash of animal substances in general, is the usual preponderance of lime over phosphorus pentoxide, and the relatively high ratio of sodium to potassium.

Ash of plants. The nature of the ash of the leaves, stems, &c., of plants is affected to a considerable extent by the composition of the soil in which the plants grow, but the amount and composition of the ash of the *seeds* are much less variable.

In nearly all seeds the largest constituents of the ash are phosphorus pentoxide and potash. In certain seeds generally used in their husk, *e.g.* oats, millet, spelt, and barley, silica is a large constituent.

But in the leaves and stems of plants, phosphorus pentoxide usually forms but a small constituent of the ash, whilst potash and lime become relatively more abundant. In cereals and grasses, silica often forms more than half of the total ash of the straw and chaff.

The following table, compiled chiefly from Wolff's analyses, gives the average proportions of ash and of its chief components in various fresh or air-dried agricultural products.
100 parts of the substance contain:—

I. *Green Fodder.*

Substance	Water	Ash	K₂O	Na₂O	MgO	CaO	P₂O₅	SO	SiO₂	Cl
Meadow grass	70·0	2·33	0·60	0·16	0·11	0·27	0·15	0·12	0·69	0·19	0·06
Rye grass .	70·0	2·13	0·53	0·09	0·05	0·16	0·17	0·08	0·84	0·11	0·07
Timothy grass	70·0	2·10	0·61	0·06	0·08	0·20	0·23	0·08	0·75	0·11	0·08
Oats, in blossom	77·0	1·66	0·65	0·06	0·05	0·11	0·14	0·05	0·55	0·07	0·04
Barley, ,,	68·0	2·25	0·59	0·01	0·07	0·14	0·22	0·07	1·08	0·08	0·07
Wheat, ,,	69·0	2·17	0·56	0·01	0·05	0·07	0·16	0·04	1·23	0·06	0·05
Rye fodder .	70·0	1·63	0·63	0·01	0·05	0·12	0·24	0·02	0·52	—	—
Red clover .	80·0	1·34	0·46	0·02	0·16	0·46	0·13	0·04	0·04	0·05	0·05
White clover .	81·0	1·36	0·24	0·11	0·14	0·44	0·20	0·12	0·06	0·04	0·06
Lucerne	75·3	1·76	0·45	0·02	0·10	0·85	0·15	0·11	0·04	0·03	0·08
Sainfoin .	78·5	1·16	0·46	0·02	0·07	0·37	0·12	0·04	0·05	0·03	—
Green vetches	82·0	1·57	0·66	0·05	0·11	0·41	0·20	0·06	0·03	0·05	0·03
Potato tops .	77·0	1·18	0·07	0·01	0·27	0·55	0·06	0·06	0·05	0·04	0·05
Mangold tops	90·7	1·48	0·43	0·31	0·14	0·17	0·08	0·11	0·07	0·17	0·05
Sugar-beet tops	89·7	1·80	0·40	0·30	0·33	0·36	0·13	0·14	0·06	0·10	—
Turnip tops .	89·8	1·40	0·32	0·11	0·06	0·45	0·13	0·14	0·05	0·12	0·05
Chicory tops .	85·0	1·87	1·12	0·01	0·06	0·27	0·17	0·17	0·02	0·03	—
Carrot tops .	80·8	2·61	0·37	0·60	0·12	0·86	0·12	0·21	0·15	0·19	0·14
Cabbage heads	88·5	1·24	0·60	0·05	0·04	0·19	0·20	0·11	0·01	0·03	0·05
Kohl-rabi tops	85·0	2·53	0·36	0·10	0·10	0·84	0·26	0·30	0·26	0·10	

II. *Hay and Straw.*

Substance	Water	Ash	K₂O	Na₂O	MgO	CaO	P₂O₅	SO	SiO₂	Cl
Meadow hay .	14·4	6·66	1·71	0·47	0·33	0·77	0·41	0·34	1·97	0·53	0·17
Red clover hay	16·0	5·65	1·95	0·09	0·69	1·92	0·56	0·17	0·15	0·21	0·21
White clover hay	16·0	6·03	1·06	0·47	0·60	1·94	0·85	0·53	0·27	0·19	0·27
Lucerne hay .	16·0	6·00	1·52	0·07	0·35	2·88	0·51	0·37	0·12	0·11	0·26
Sainfoin hay .	16·0	4·53	1·79	0·08	0·26	1·46	0·47	0·15	0·18	0·14	
Oat hay	14·5	6·18	2·41	0·20	0·20	0·41	0·51	0·17	2·05	0·25	0·15
Wheat straw .	14·1	4·26	0·49	0·12	0·11	0·26	0·23	0·12	2·82	—	0·16
Rye straw .	15·4	4·07	0·76	0·13	0·13	0·31	0·19	0·08	2·37		0·09
Barley straw .	14·0	4·39	0·93	0·20	0·11	0·33	0·19	0·16	2·36		0·13
Oat straw .	14·1	4·40	0·97	0·23	0·18	0·36	0·18	0·15	2·11		0·17
Maize straw .	14·0	4·72	1·66	0·05	0·26	0·50	0·38	0·25	1·79		0·39
Pea straw .	14·3	4·92	1·07	0·26	0·38	1·86	0·38	0·28	0·28	0·30	0·07
Field bean straw	18·0	5·84	2·59	0·22	0·46	1·35	0·41	0·01	0·31	0·81	0·22
Buckwheat straw	16·0	5·17	2·41	0·11	0·19	0·95	0·61	0·27	0·28	0·40	—
Flax straw .	14·0	3·19	1·18	0·16	0·23	0·83	0·43	0·20	0·22	0·15	0·14
Flax, whole plant	25·0	3·23	1·13	0·15	0·29	0·50	0·74	0·16	0·08	0·19	—
Hop, ,, ,,	25·0	7·40	1·94	0·28	0·43	1·18	0·90	0·38	1·59	0·34	0·20
Hops . .	12·0	5·98	2·23	0·13	0·21	1·01	0·90	0·16	0·92	0·02	0·48
Tobacco .	18·0	19·75	5·41	0·73	2·07	7·31	0·71	0·77	1·92	0·88	
Heather .	20·0	3·61	0·48	0·19	0·30	0·68	0·18	0·16	1·27	0·08	
Broom . .	16·0	4·89	0·69	0·05	0·28	0·32	0·16	0·07	0·19	0·05	
Fern . .	16·0	5·89	2·52	0·27	0·45	0·83	0·57	0·30	0·36	0·60	
Reeds . .	18·0	3·85	0·33	0·01	0·05	0·23	0·08	0·11	2·75	—	
Sedge . .	14·0	6·95	2·31	0·51	0·29	0·37	0·47	0·23	2·18	0·39	
Rush . .	14·0	4·56	1·67	0·30	0·29	0·43	0·29	0·40	0·50	0·65	

III. *Root Crops.*

Substance	Water	Ash	K₂O	Na₂O	MgO	CaO	P₂O₅	SO	SiO₂	Cl
Potato .	75·0	0·94	0·56	0·01	0·04	0·02	0·18	0·06	0·02	0·03	0·02
Artichoke .	80·0	1·03	0·67	—	0·03	0·04	0·16	0·03	—	0·02	—
Mangold .	88·3	0·80	0·43	0·12	0·04	0·04	0·08	0·03	0·02	0·05	0·02
Sugar beet .	81·6	0·80	0·40	0·08	0·07	0·05	0·11	0·04	0·03	0·02	—
Turnip .	90·9	0·75	0·30	0·08	0·03	0·08	0·10	0·11	0·02	0·03	0·04
White turnip	91·5	0·61	0·31	0·02	0·02	0·08	0·11	0·04	0·01	0·04	—
Kohl-rabi .	87·7	0·95	0·49	0·06	0·02	0·09	0·14	0·08	0·01	0·05	—
Carrot .	86·0	0·88	0·32	0·19	0·05	0·09	0·11	0·06	0·02	0·03	0·01
Chicory .	80·0	1·04	0·42	0·08	0·07	0·09	0·15	0·10	0·06	0·04	

Substance	Water	Ash	K$_2$O	Na$_2$O	MgO	CaO	P$_2$O$_5$	SO$_3$	SiO$_2$	Cl
IV. _Grains and Seeds._										
Wheat .	14·3	1·77	0·55	0·06	0·22	0·06	0·82	0·04	0·03	—	0·15
Rye .	14·9	1·73	0·54	0·03	0·19	0·05	0·82	0·04	0·03	—	0·17
Barley .	14·5	2·18	0·48	0·06	0·18	0·05	0·72	0·05	0·59	—	0·14
Oats .	14·0	2·64	0·42	0·10	0·18	0·10	0·55	0·04	1·23	—	0·17
Spelt .	14·8	3·58	0·62	0·06	0·21	0·09	0·72	0·06	1·58	—	—
Maize .	13·6	1·23	0·33	0·02	0·18	0·03	0·55	0·01	0·03	—	0·12
Sorghum	14·0	1·60	0·42	0·05	0·24	0·02	0·81	—	0·12	—	—
Millet .	13·0	3·90	0·47	0·04	0·33	0·04	0·91	0·01	2·05	—	0·18
Paddy rice	12·0	6·90	1·27	0·31	0·59	0·35	3·26	0·04	0·04	—	—
Rice .	13·0	0·34	0·08	0·02	0·05	0·01	0·17	—	0·01	—	—
Buckwheat	14·1	0·92	0·21	0·06	0·12	0·03	0·44	0·02	—	0·02	—
Flax seed	11·8	3·22	1·04	0·06	0·42	0·27	1·30	0·04	0·04	—	0·17
Peas .	13·8	2·42	0·98	0·09	0·19	0·12	0·88	0·08	0·02	0·06	0·24
Field beans	14·1	2·96	1·20	0·04	0·20	0·15	1·16	0·15	0·04	0·08	0·23
V. _Fruits, &c._										
Apple, whole fruit	84·0	0·27	0·10	0·07	0·02	0·01	0·04	0·02	0·01	—
Pear, ,, ,,	80·0	0·41	0·22	0·04	0·02	0·03	0·06	0·02	0·01	—
Cherry, ,, ,,	78·0	0·43	0·22	0·01	0·02	0·03	0·07	0·02	0·04	0·01
Plum, ,, ,,	82·0	0·40	0·24	—	0·02	0·04	0·06	0·02	0·01	—
Acorns, fresh	56·0	0·96	0·62	0·01	0·05	0·07	0·16	0·05	0·02	0·01
Beech mast .	18·0	2·71	0·62	0·27	0·31	0·67	0·56	0·06	0·05	0·01
Horse chestnuts	49·2	1·20	0·71	—	0·01	0·14	0·27	0·02	—	0·08
VI. _Leaves—Autumn._										
Mulberry . .	67·0	1·17	0·23	—	0·06	0·30	0·12	0·01	0·41	—
Horse chestnut .	60·0	3·01	0·59	—	0·24	1·22	0·25	0·05	0·42	0·12
Walnut .	60·0	2·84	0·76	—	0·28	1·53	0·11	0·08	0·06	0·02
Beech . . .	55·0	3·05	0·16	0·02	0·18	1·37	0·13	0·11	1·03	0·01
Oak . .	60·0	1·96	0·07	0·01	0·08	0·95	0·16	0·09	0·61	—
Scotch fir .	55·0	0·63	0·06	—	0·06	0·26	0·13	0·03	0·08	0·03
Spruce . .	55·0	2·63	0·04	—	0·06	0·40	0·21	0·07	1·84	—
VII. _Manufactured Products._										
Fine wheat flour .	13·6	0·41	0·15	0·01	0·03	0·01	0·21	—	—	—
Wheat bran .	13·5	5·56	1·33	0·03	0·94	0·26	2·88	—	0·06	—
Rye flour .	14·2	1·69	0·65	0·03	0·14	0·02	0·85	—	—	—
Rye bran .	13·1	7·14	1·93	0·09	1·13	0·25	3·42	—	—	—
Barley flour .	14·0	2·00	0·58	0·05	0·27	0·06	0·95	0·06	—	—
Maize meal .	14·0	0·95	0·27	0·03	0·14	0·06	0·43	—	—	—
Malt . .	4·2	2·66	0·46	—	0·22	0·10	1·07	—	0·88	—
Malt dust .	9·2	5·96	2·08	—	0·08	0·09	1·25	0·38	1·77	—
Beer . .	90·0	0·39	0·15	0·03	0·02	0·01	0·13	0·01	0·04	0·01
Wine . .	86·6	0·28	0·18	—	0·02	0·02	0·05	0·01	0·01	—
Linseed cake .	11·5	5·52	1·29	0·08	0·88	0·47	1·94	0·19	0·36	0·03
Cotton-seed cake	11·5	6·15	2·18	—	0·26	0·28	2·95	0·07	0·25	—
Potato skins .	30·0	6·71	4·83	0·05	0·45	0·64	0·23	0·03	0·18	0·14
Buckwheat groats	14·0	0·62	0·16	0·04	0·08	0·01	0·30	0·01	—	0·01
VIII. _Wood (air-dried)._										
Apple tree .	15·0	1·10	0·13	0·02	0·06	0·78	0·05	0·03	0·02	—
Beech, trunk	15·0	0·55	0·09	0·02	0·06	0·31	0·03	0·01	0·03	—
Beech, brushwood .	15·0	1·23	0·17	0·03	0·13	0·59	0·15	0·01	0·12	—
Birch . .	15·0	0·26	0·03	0·02	0·02	0·15	0·02	—	0·01	—
Grape . .	15·0	2·34	0·70	0·16	0·16	0·87	0·30	0·06	0·02	0·02
Mulberry .	15·0	1·37	0·09	0·20	0·08	0·78	0·03	0·14	0·05	0·06
Larch . .	15·0	0·27	0·04	0·02	0·07	0·07	0·01	0·01	0·01	—
Oak . .	15·0	0·51	0·05	0·02	0·02	0·37	0·03	0·01	0·01	—
Scotch fir .	15·0	0·26	0·03	0·01	0·02	0·13	0·02	0·01	0·04	—

In addition to the constituents given in the above table, small quantities of oxides of iron and manganese are almost invariably present in vegetable ashes.

Titanium (Wait, J. Amer. Chem. Soc. 1896, 18, 402), aluminium, fluorine, and boron (Crampton, Amer. Chem. J. 11, 227; Jay, Compt. rend. 121, 893; Baumert, Ber. 21, 3290), are also frequently present in small quantities in the ash of certain plants.

Lithium, rubidium, zinc, copper, barium, and arsenic have also been detected in the ash of certain plants grown in soils containing these constituents (Passerini, Chem. Soc. Abstr. 1893, ii. 225; Homberger, *ibid.* 1899, A, ii. 506; Macdougal, *ibid.* 1900, A, ii. 235).

Even chromium, molybdenum, and vanadium have been detected in the ash of fir, oak, vine, and poplar (Demarcay, *ibid.* 1900, 235).

Indeed, the composition of the soil has a great influence upon the amount and composition of the ash of the crop grown upon it, though this influence is much more marked upon the foliage, stem, &c., than upon the seed.

Certain plants, originating from plants of the seashore, *e.g.* asparagus, beet, and carrot, generally leave an ash containing unusually high amounts of chlorine and sodium, and application of common salt as manure to such crops is usually stated to be beneficial, although on no very sufficient evidence.

Plants like salt-worts (*Salsola*) and samphire (*Salicornia*) growing on the coast, contain relatively enormous quantities of soda—in the former 6 times, in the latter 14 times, as much soda as of potash.

The ash of the club-moss (*Lycopodium*) contains from 20 to 50 p.c. of alumina.

As already stated, some of the phosphates and sulphates found in the ash of plants result from the oxidation of phosphorus and sulphur organic compounds present in the original plant.

Posternak (Compt. rend. 137, 1903) detected the existence in peas, beans, potatoes, and the seeds of the red fir, pumpkin, white and yellow lupines of *anhydro-oxymethylene diphosphoric acid*—

$$O<^{CH_2—OPO(OH)_2}_{CH_2—OPO(OH)_2}$$
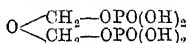
Patten and Hart (Bull. 250 (1904), N. York Agric. Expt. Station) have shown that about 86 p.c. of the total phosphorus in bran, 81 p.c. in malt sprouts, and 50 p.c. in oats, is soluble in 0·2 p.c. sol. of hydrochloric acid; and that the greater portion of this is present in the bran as calcium, magnesium and potassium salts of anhydro-oxymethylene diphosphoric acid.

Importance of the Ash Constituents of Foods.

The influence of the mineral matter in the food of animals upon their health and well-being is probably much greater than is generally recognised. Not only is it essential that all the inorganic constituents required for building up the tissues and producing the various digestive and other secretions be supplied in sufficient quantities, but it is important, at least with certain pairs of constituents, that they be supplied in appropriate ratios to each other.

A preponderance of phosphoric acid over lime and magnesia in the diet is probably the cause or a predisposing cause of certain diseases of the bones of horses, mules, and donkeys (Ingle, Jour. Comp. Pathology and Therapeutics, 1907; Jour. Agric. Science, 1908, iii. 22; Jour. Roy. Inst. Public Health, 1909); while the ratio of potash to soda in the food has an important bearing upon health, and especially upon the susceptibility to certain diseases, *e.g.* scurvy.

The cereals contain a large excess of phosphoric acid over lime, and the use of an exclusively cereal diet may lead to imperfect bone nutrition (*l.c.*; also Illustrated Poultry Record, 1910).

The necessity of an adequate supply of chlorides in the diet is well recognised, and in many countries the ordinary food supplies of domestic animals have to be supplemented by common salt to ensure healthy existence.

Whenever the rations are restricted to one or two items, there is considerable probability that certain mineral constituents will be lacking or supplied in improper proportions.

It is too often the practice, in discussing the feeding of animals, to devote much consideration to the organic portions of their food, but beyond requiring that sufficient mineral matter or 'bone-forming' material be present, to pay little or no attention to its composition.

Thus bran is widely regarded as a food particularly rich in mineral matter, and therefore valuable for bone nutrition; but the ratio of phosphorus pentoxide to lime in this food is about 11 to 1, and the practice of feeding animals largely upon bran is known to produce a disease of the bones—'bran rachitis' in horses.

Kellner (Scientific Feeding of Animals, 1909) estimates that for oxen, 50 grams of phosphorus pentoxide and 100 grams of lime per 1000 kilos. body weight per day, are required in the food, while for full-grown sheep, 1 gram of the former and 11 grams of lime suffice.

In England, fortunately, hay—either meadow or clover—forms a large part of the rations of farm animals, and this contains a large excess of lime over phosphoric acid, and thus neutralises the opposite preponderance in the grain or cake used with it.

But in South Africa and perhaps some other countries, meadow or clover hay is but little used, and many horses are fed entirely upon oat hay or oat hay and maize. In either case there is a large preponderance of phosphoric acid over lime, and to this fact the prevalence of certain bone diseases is almost certainly due.

Similar considerations apply to other animals kept in confinement, especially to poultry when deprived of a grass run, and to pigs. H. I.

ASPARAGINE. *Aminosuccinamic acid* $C_2H_3·NH_2(CO_2H)(CO·NH_2)$ occurs in two optically active forms, differing in direction of rotatory power and in taste. *Lævo-asparagine*, discovered by Vauquelin and Robiquet (Ann. Chim. anal. 1805, 57, ss. in the young shoots of asparagus (*Asparagus officinalis*, Linn.), is widely distributed in the vegetable kingdom, occurring in most plants at the time of budding and during the flowering period, and, with glutamine, forms the chief non-proteid compounds present in the juice of ripening oranges (Scurti and de Plato, Chem. Zentr. 1908, ii. 16, 1370). Miyacha (Bull. Coll. Agric. Imp. Univ. Tokyo, 1897, 2, 458) has shown that in the cases of *Pæonia albiflora* and *Thea chinensis*, even old leaves, showing incipient decay, can produce asparagine. It occurs to a larger extent in leguminous plants than in any other natural order, and is most abundant at the time of germination, the quantity being greater in etiolated than in normal plants (Borodin, Bied. Zentr. 1879, 357),

Sachsse (Landsw. Versuchs. Stat. 1874, 17, 88) found that the amount of asparagine in germinating peas increased from 0·67 to 6·94 p.c. during 24 days' growth; and Schulze and Umlauft (*ibid.* 1875, 18, 1) found 17·9 p.c. of asparagine in the dried shoots of *Lupinus luteus* seedlings germinated in the dark in distilled water (compare also Mercadante, Gazz. ital. chim. 1875, 5, 187 ; Schulze, Landsw. Versuchs. Stat. 1895, 46, 383 ; Stoklasa, Landw. Jahrb. 1895, 24, 827 ; Bourquelot and Herissey, J. Pharm. 1898, (vi.) 8, 385 ; Bréal, Ann. Agron. 1900, 26, 5 ; Schulze and Barbieri, Landsw. Versuchs. Stat. 21, 63 ; Kinoshita, Bull. Coll. Agric. Imp. Univ. Tokyo, 1895, 2, 203) ; Schulze and Bosshard, Zeitsch. physiol. Chem. 1885, 9, 420 ; Bungener, Bied. Zentr. 1885, 861 ; Behrens, Bot. Zentr. 1894, 178). Asparagine is one of the decomposition products of proteid matter (Schulze, Bied. Zentr. 1901, 30, 106 ; Chem. Zentr. 1901, i. 1108 ; Ber. Deut. Bot. Ges. 1907, 25, 213), and its accumulation in the plant during the periods of germination and budding, particularly when the development occurs in the dark is attributed by Borodin (Bied. Zentr. 1879, 357) and Schulze and Barbieri (J. pr. Chem. 1882, [2] 25, 145), to the absence of carbohydrates which under conditions of normal assimilation effect the reincorporation of amides into proteid molecules ; and this view is confirmed by Monteverde (Ann. Agron. 17, 376), who found that branches of lilac plunged in distilled water or 4 p.c. glycerol solution and kept in the dark, contained abundance of asparagine at the end of 15 days, but neither starch nor mannitol. When, however, branches of the same plant were kept in solutions of glucose, sucrose, or mannitol, they formed no asparagine in a month, but contained much mannitol and starch. Another source of asparagine in the plant is its synthetic formation from ammonium salts, urea, or nitrates supplied by the soil. This synthetic production is only possible in the presence of sugar, and under conditions that exclude the formation of proteids (Suzuki, Bull. Coll. Agric. Imp. Univ. Tokyo, 1895, 2, 196). The function of the asparagine in the plant economy is the production of proteid matter ; hence the addition of leguminous seeds after steaming to the mash in brewing is recommended by Birner (J. Soc. Chem. Ind. 1882, 333), as the asparagine they yield forms excellent nutriment for the yeast cell ; and Kinoshita (Bull. Coll. Agric. Imp. Univ. Tohyo, 1895, 2, 196) found that young shoots of soja bean that showed an increase in asparagine, from 21·5 to 28·7 p.c. after four weeks' natural growth, became poorer in asparagine (18·9–13·7 p.c.) if grown for the same period in methyl alcohol and glycerol solution, but contained reserve proteid matter.

Asparagine can be extracted from the juice expressed from young vetch seedlings that have germinated in the dark, 10 kilos. of vetch yielding 150 grams of pure asparagine (Piria, Annalen, 1848, 68, 343).

Asparagine crystallises from aqueous solution in large rhombic lævo- hemihedral prisms, $a : b : c : : 0.4752 : 1 : 0.8294$ (Freundler, Compt. rend. 1897, 125, 657), containing $1H_2O$, which it loses at 100°, and then melts at 234°–235° (Michael, Ber. 1895, 28, 1629) ; it has a sp.gr. 1·5434 at 14·8°/4° (Piutti, Gazz. ital. chim. 1904,

34, 36) ; the molecular heat of combustion is 448·4 Cals., and the heat of formation 205·1 Cals. (Berthelot and Andre, Compt. rend. 1890, 120, 884) ; it is sparingly soluble in cold, readily so in hot water—1 part dissolves in 82 parts of water at 10°, in 47 parts at 20° (Becker, Ber. 1881, 14, 1028), in 58 parts at 13°, and 1·89 parts at 100° (Guareschi, Gazz. chim. ital. 1876, 6, 370 ; compare Bresler, Zeitsch. physikal. Chem. 1904, 47, 611). The aqueous solution is weakly acid, has an insipid and disagreeable taste, and is lævo-rotatory $[a]_D - 5°$ 4' (Piutti, Compt. rend. 1886, 103, 134) ; the rotatory power of the solution is increased by the addition of alkalis, inverted by mineral acids, and destroyed by acetic acid (Champion and Pellet, Compt. rend. 1876, 82, 819 ; Becker, Ber. 1881, 14, 1028). Advantage is taken of this last fact to eliminate the error due to the presence of asparagine in saccharimetric determinations of sugar liquors from beets and canes. Asparagine is partially hydrolysed by boiling with water, forming *aspartic acid (aminosuccinic acid)* $C_2H_3 \cdot NH_2(CO_2H)_2$ and ammonia ; the change is rapid and complete when excess of barium hydroxide or dilute hydrochloric or sulphuric acid is employed (Schulze, Landsw. Versuchs. Stat. 29, 233) ; by the action of potassium permanganate, asparagine is oxidised to carbamide and ammonia ; and when used in 5 p.c. aqueous solution for the culture of *Bacillus pyrocyanicus*, it is converted into aspartic acid after 60 hours, and completely decomposed after 72 hours (Arnaud and Charrin, Compt. rend. 1891, 112, 755 ; Adeney, Proc. Roy. Irish Acad. 1905, 25, 6). Under the action of enzymes, asparagine yields a mixture of formic, propionic, and succinic acids (Neuberg and Cappezzuoli, Biochem. Zeitsch. 1909, 18, 424), and a similar change is effected by brewer's yeast (Effront, Mon. Sci. 1909, (iv.) 23, i. 145).

The estimation of asparagine is based upon its quantitative conversion into aspartic acid and ammonia by the action of hydrochloric acid, the aspartic acid may be removed in the form of its sparingly soluble copper salt (Engel, Compt. rend. 1888, 106, 1734) and the ammonia determined by Sachsse's method (J. pr. Chem. 1872, [2] 6, 118) or by one of the modifications of Schloessing's method described by Meunier (Ann. Agron. 6, 275), by Schulze (J. pr. Chem. 1885, [2] 31, 233), or by Brown and Millar (Jour. Soc. Chem. Ind. 1904, 135).

Asparagine has feeble basic and acidic properties, and forms salts with acids and bases (Chautard and Dessaigne, Annalen, 1848, 68, 349 ; Dessaigne, Annalen, 1852, 82, 237 ; Smolka, Monatsh. 1887, 6, 915) ; it also forms double compounds with certain salts of the heavy metals, the sparing solubility of the compound with mercuric nitrate is made use of in isolating small quantities of asparagine from solutions containing carbohydrates (Schulze, Ber. 1882, 15, 2855) ; the *alum* $(C_4H_8O_3N_2)_2H_2SO_4,Al_2(SO_4)_3,24H_2O$ forms octahedral crystals. Asparagine is converted into *l*-chlorosuccinic acid and fumaric acid by the action of nitrosyl chloride in hydrochloric acid solution (Tilden and Forster, Chem. Soc.

Trans. 1895, 67, 489); it yields the amide of uramidosuccinic anhydride
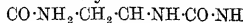
$$CO \cdot NH_2 \cdot CH_2 \cdot CH \cdot NH \cdot CO \cdot NH$$
$$\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\quad CO-$$

when fused with carbamide (Guareschi, Gazz. ital. chim. 1876, 6, 370), and is converted into amidosuccinuric acid

$$CONH_2 \cdot CH_2 \cdot CH \diagdown {NH \cdot CO \cdot NH_2 \atop COOH}$$
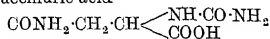
m.p. 137°–138°, by the action of potassium cyanate (Guareschi, Ber. 1877, 10, 1747). Certain condensation products of asparagine with other amino- acids are described by Fischer (Ber. 1904, 37, 4585; 1907, 40, 2048), *chloroacetylasparagine*, m.p. 148°–149° (corr.); *glycylasparagine*, m.p. 216°, $[a]_D -6\cdot4°$ at 20°; *anhydroglycylasparagine*, decomposing at 274°; *d-leucyl-l-asparagine*, decomposing at 230° (corr.), $[a]_D -53\cdot6°$ at 20°; *l-leucyl-d-asparagine*, m.p. 228° (corr.), $[a]_D +17\cdot8°$; *asparagylaspartic acid*, decomposing at 120°. Sasaki (Beitr. Chem. Physiol. Path. 1907, 10, 120) describes a *benzoylpolypeptide* of asparagine $C_{19}H_{24}O_8N_6$, decomposing at 210°, and giving the biuret reaction.

As regards the alimentary value of asparagine, it has been found that in the case of herbivorous mammals and geese, asparagine has a proteidsparing action, and under appropriate conditions prevents waste and causes the formation of proteid matter (Weiske, Bied. Zentr. 1879, 744; 1882, 312; Zeit. für Biol. 15, 261; 20, 276; Landws. Versuchs. Stat. 1888, 34, 303; Rosenfeld, Zeit. Ver. Deutsch. Zucker. Ind. 1900, [539] 1055, from Jour. Soc. Chem. Ind. 1901, 271). According to Zuntz and Müller (Pflüger's Archiv. 1906, 112, 245), the proteidsparing action of asparagine is the result of a kind of symbiosis, the bacteria in the paunch of the ruminants decomposing the asparagine in preference to the protein in the food. In the case of omnivora and carnivora, asparagine exerts only a diuretic action (Murck and Voit, Bied. Zentr. 1884, 749; Politis, Zeit. Biol. 1893, 27, 492; Mauthner, *ibid.* 507; Gabriel and Voit, *ibid.* 29, 115, 125; Levena and Kohn, Amer. Jour. Physiol. 1909, 23, 324).

Dextro-asparagine was discovered by Piutti (Ber. 1886, 19, 1691) in the young shoots of the vetch (*Vicia sativa*, Linn.) 6500 kilos. of vetch buds yielded 20 kilos. of crude asparagine, from which 100 grams of pure dextro-asparagine was isolated; it is slightly more soluble than the lævo- compound; the solution has an intensely sweet taste, is dextro-rotatory in neutral or alkaline solution $[a]_D +5\cdot41°$ (Piutti, Compt. rend. 1886, 103, 134), and lævo-rotatory in acid solution; it forms large rhombic dextrohemihedral crystals, $a : b : c : : 0\cdot4741 : 1 : 0\cdot8310$ (Freundler, Compt. rend. 1897, 125, 657). A solution of equal parts of the two optically active asparagines is optically inactive, but the two varieties separate on crystallisation, twining frequently taking place between the left and right crystals (Piutti, Compt. rend. 1886, 103, 134).

According to Pringsheim (Zeitsch. physiol. Chem. 1910, 65, 89), the *d*-asparagine found by Piutti is the mother liquors from which the *l*-asparagine had been isolated, was formed by the racemisation of the *l*-asparagine during the process of evaporation of the solutions. The author states that after boiling *l*-asparagine $[[a]_D^{20°} +36\cdot19°$, in $N/10$ hydrochloric acid solution] for 12 hours, with water, and subsequent fractional crystallisation, he obtained a fraction that had $[a]_D^{20°} -15\cdot3°$ in $N/10$ hydrochloric acid solution, and therefore contained *d*-asparagine.

In addition to the two asparagines already described, there is a third form known as *a*-asparagine; it does not occur naturally; is optically inactive, crystallises in the triclinic system, $a : b : c = 1\cdot5957 : 1 : 0\cdot5668$; $a = 91°19'$; $\beta = 113°/12'$, $\gamma = 83°$ 48' (Brugnatelli); and has a sp.gr. 1·454 at 14·8°/4° (Piutti, Gazz. chim. ital. 1904, 34, ii. 36), and is not structurally identical with the optically active or β-asparagines. The three asparagines have been synthesised by Piutti (Gazz. chim. ital. 1887, 17, 126; 1888, 18, 457) by the following methods, that leave no doubt as to the constitution of the compounds. By the reduction of the oxime of oxalacetic ester $CO_2Et \cdot CH_2 \cdot C(NOH) \cdot CO_2Et$ with sodium amalgam and partial saponification of the product, Piutti obtained two different ethyl hydrogen aspartates, melting at 165° and 200° respectively. The ester melting at 165° is identical with the compound obtained by reducing Ebert's (Annalen, 1885, 229, 45) monoethyl ester of oximinosuccinic acid, which has the formula $CO_2H \cdot CH_2 \cdot C(NOH) \cdot CO_2Et$, since on heating it loses CO_2 and forms oximinopropionic ester $CH_2 \cdot C(NOH) \cdot CO_2Et$. It follows, therefore, that the ethyl hydrogen aspartate melting at 165° is the monoethyl a-aspartate $CO_2H \cdot CH_2 \cdot CH(NH_2) \cdot CO_2Et$, and the ester melting at 200° must be the monoethyl β-aspartate $CO_2H \cdot CH(NH_2)CH_2 \cdot CO_2Et$. When these esters are treated with alcoholic ammonia, they are converted into the corresponding asparagines; the ester m.p. 165° gives inactive *a-asparagine* $CO_2H \cdot CH_2 \cdot CH(NH_2) \cdot CONH_2$, and the ester m.p. 200° yields a mixture of *d*- and *l*- β-asparagines $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CONH_2$. From silver ethyl γ-oximinosuccinate

$$OH \cdot N \diagdown {CH \cdot CO_2Et \atop CH \cdot CO_2Ag}$$
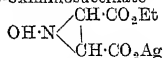
Piutti (Gazz. chim. ital. 1890, 20, 402) obtained a mixture of the three asparagines, the a-asparagine readily gave up its water of crystallisation in a vacuum, and fell to powder; and the *d*- and *l*- β-asparagines could then be separated by hand sorting. A mixture of the three asparagines was also obtained by the action of alcoholic ammonia on the ethyl hydrogen ester of inactive aspartic acid (Piutti, Gazz. ital. chim. 1887, 17, 126; 1888, 18, 457). Körner and Menozzi (Gazz. ital. chim. 1887, 17, 171, 226) effected the synthesis of the *d*- and *l*- β-asparagines from ethyl bromosuccinate, from ethyl fumarate or ethyl maleate, by the action of alcoholic ammonia; and similar results were obtained by Piutti (Ber. 1896, 29, 2069) with *l*-bromosuccinamic acid or maleic anhydride.

β-Ethylasparagine $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO \cdot NHEt$, m.p. 258°–260°, with decomposition, and *β-allylasparagine* $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO \cdot NH \cdot C_3H_4$, melting and decomposing at 258°–261°, prepared by the action of the corresponding alkylamine on β-ethylaspartic acid,

yield optically inactive solutions (Piutti, Gazz. chim. ital. 1888, 18, 478).　　　M. A. W.

ASPARAGUS. The shoots of this plant (*Asparagus officinalis*) are used as a table vegetable.

	Carbo-			
		Water	Protein	Fat	hydrates	Ash
Average composition	94·0	1·8	0·2	3·3	0·7

The nitrogenous matter of asparagus consists largely of *amino-succinamic acid* $CO(NH_2)\cdot CH_2\cdot CH(NH_2)\cdot COOH$, a substance known (from its discovery, in 1805, in asparagus shoots) as *asparagine* (*q.v.*).

Coniferin and vanillin have also been found in the sap and cellular tissue (Lippmann, Ber. 1886, 18, 3355); Tanret (Compt. rend. 1909, 149, 48) describes two new carbohydrates as occurring in approximately equal quantities in asparagus roots—*asparagose* $(C_6H_{10}O_5)_n\cdot H_2O$, where $n=15$ or 16, crystallising in microscopic needles, soluble in water, insoluble in absolute alcohol, m.p. 198°–200°, gives no colouration with iodine, and does not reduce Fehling's solution; and *ψ-asparagose*, a white, hygroscopic substance more soluble than asparagose. Both substances are hydrolysed by invertase, yielding dextrose and lævulose.

The seeds of asparagus were examined by Peters (Arch. Pharm. 1902, 240, 53), and were found to contain water 11·5, woody fibre 8·2, nitrogen 3·0, and oil 15·3 p.c. Starch was not present, but a reserve cellulose (mannan), capable of yielding *d*-mannose on boiling with dilute hydrochloric acid, occurred ; 37·5 p.c. of the weight of the seeds, of mannose was obtained. The oil was reddish yellow, had a sp.gr. of 0·928 at 15°, and an iodine number of 137·1. H. I.

ASPARTIC ACID. *Aminosuccinic acid* $CO_2H\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, found in young sugar cane and in molasses of sugar beet (Scheibler, J. 1886, 399), and in young shoots of the gourd (Schulze and Barbieri, Ber. 1878, 11, 710), has been observed in diseased liver (Taylor, Zeitsch. physiol. Chem. 1901, 34, 580), and occurs in certain glands of *Tritonium nodosum*, the posterior portion of the gland when stimulated secretes an acid fluid from which aspartic acid immediately crystallises. As aspartic acid is soluble in sea-water, it is probably employed by the animal in destroying the calcareous shells of the other shellfish that form its food (Henze, Ber. 1901, 34, 348).

Aspartic acid is prepared by hydrolysing asparagine by means of hydrochloric or sulphuric acid, lime, baryta, lead oxide or potash (Plisson, Ann. Chim. Phys. [2] 35, 175 ; 37, 81 ; 40, 303 ; Schulze, Landsw. Versuchs. Stat. 29, 233) ; it is one of the degradation products of proteid matter, and is obtained when casein or proteid is heated with (1) dilute sulphuric acid (Kreussler, J. pr. Chem. 1869, 107, 239 ; Ritthausen, *ibid.* 218 ; Fischer, Zeitsch. physiol. Chem. 1901, 33, 151 ; 1902, 35, 70 ; 36, 462) ; (2) bromine or with stannous chloride (Hlasiwetz and Habermann, Annalen, 1871, 159, 325 ; 1873, 169, 162). Aspartic acid is produced by the oxidation of conglutin with potassium permanganate (Pott, J. pr. Chem. 1873, [2] 6, 91), by the pancreatic digestion of fresh blood fibrin at 40°–50° (Radziezewski and Salkowski, Ber. 1874, 7, 1050), or of gluten (Knieriem, Zeitsch. f. Biol 1876, 11, 198); and

is one of the acid constituents of Kühne's ' antipeptone ' (Kutscher, Zeitsch. physiol. Chem. 1898, 25, 195 ; 26, 110).

The naturally occurring aspartic acid is lævo-rotatory and the same *l-aspartic acid* is obtained by hydrolysis of *lævo*-asparagine (Schiff, Ber. 1884, 17, 2929); it crystallises in rhombic prisms, m.p. 270°–271° (Michael, Ber. 1895, 28, 1629), is sparingly soluble in water, 100 grams of water dissolve y mg. of the acid at $t°$, where

$$y=372+14\cdot1t--0\cdot18124t^2+0\cdot0053t^3$$

(Engel, Compt. rend. 1888, 106, 1734). A solution containing 1·873 p.c. of acid is feebly dextro-rotatory below 75°, but lævo-rotatory above that temperature ; in alkaline solutions the substance is strongly lævo-, and in acids strongly dextro-, rotatory (Becker, Ber. 1881, 14, 1028). The heat of combustion is 387·2 Cals., the heat of formation 231·9 Cals. (Berthelot and André, Compt. rend. 1890, 110, 884) ; the heat of dissolution at 16° is --7·25 Cals., heat of neutralisation by sodium hydroxide +3·0 Cals. for the first, and +3·5 Cals. for the second equivalent (Berthelot, Compt. rend. 1891, 112, 829). Aspartic acid is readily soluble in aqueous solutions of certain mineral salts ; for this reason Schiff (Ber. 1886, 17, 2929) recommends that in its preparation from asparagine by boiling with hydrochloric acid, the minimum quantity (2 mols.) of acid be employed, and the excess afterwards neutralised by ammonia (1 mol.); by adopting this precaution, a yield of 90 p.c. of the theoretical is obtained.

Aspartic acid forms salts with acid and bases, the copper salt $C_4H_5O_4NCu,4\frac{1}{2}H_2O$, forms pale-blue needles almost insoluble in cold water (Engel, *l.c.*). Aspartic acid is oxidised by hydrogen peroxide to the semi-aldehyde of malonic acid which breaks up into acetaldehyde and carbon dioxide (Dakin, Jour. Biol. Chem. 1909, 5, 409) ; it is capable of furnishing the nitrogen required for the development of *B-coli communis* in presence of mannitol and glucose, becoming reduced to ammonium succinate (Harden, Chem. Soc. Trans. 1901, 623), and by enzyme action it is decomposed into formic, propionic, and succinic acids (Neuberg and Cappezzuoli, Biochem. Zeitsch. 1909, 18, 424 ; Borchardt, Zeitsch. physiol. Chem. 1909, 59, 96). When aspartic acid is heated at 190°–200° for 20 hours, and the product boiled with water, two sparingly soluble anhydrides, *octoaspartide*

$$\underset{|}{NH-} $$
$$HO(CO\cdot C\cdot CH_2\cdot CO)_8H$$
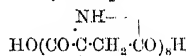
and *tetraspartide*

$$NH---- $$
$$HO(CO\cdot C\cdot CH_2\cdot CO)_4H$$
$$|$$
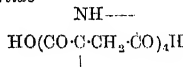
are obtained, the more soluble *octoaspartic*

$$NH_2 $$
$$HO(CO\cdot C\cdot CH_2\cdot CO_2H)_8H$$
$$|$$
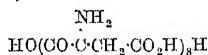
and *tetraspartic acid*

$$NH_2 $$
$$HO(CO\cdot C\cdot CH_2\cdot CO_2H)_4H$$
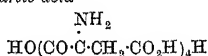
can be isolated from the filtrate (Schiff, Ber. 1897, 30, 2449). The following alkyl esters of aspartic acid are described: *Monoethyl asparate hydrochloride*, m.p. 199°; *diethyl* and *dimethyl aspartate hydrochlorides*, deliquescent solids (Curtius and Koch, Ber. 1885, 18, 1293; Wegscheiden and Frankl,Monatsh. 1906, 27, 487), *ethyl β-aspartate* $CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot CO_2Et$, m.p. 200°; *ethyl α-aspartate* $CO_2H \cdot CH_2 \cdot CH(NH_2) CO_2Et$, m.p. 165° (Piutti, Chem. Zentr. 1888, 1459). The methyl, ethyl, allyl, propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl hydrogen esters are dextro-rotatory at ordinary and lævo-rotatory at higher temperatures, and form sparingly soluble copper salts (Piutti and Maghi, Gazz. chim. ital. 1906, 36, ii. 738). *l*-Diethylaspartate has b.p. 126·5°/11 mm. pressure; sp.gr. 1·089 at 17° and $[a]_D^{20°} = -9·46°$ (Fischer, Sitzungber., Akad. Wiss. Berlin, 1900, 48, 1062), or b.p.126°–127°/10 mm., 150°–152°/25 mm. pressure, and forms a yellow *picrolonate* $C_8H_{15}O_4N,C_{10}H_8O_5N_4$, m.p. 290° (Schmidt and Widman, Ber. 1909, 42, 497).

Of the *acyl* derivatives of aspartic acid, the *benzenesulphonyl* derivative $SO_2Ph \cdot NH \cdot C_2H_3 (CO_2H)_2$ melts at 170° (Hedin, Ber. 1891, 23, 3196); the *hippuryl* derivative $NHBz \cdot CH_2 \cdot CO. NH \cdot C_2H_3(CO_2H)_2$, m.p. 191° (Curtius and Curtius, J. pr. Chem. 1904; (ii.) 70, 158); *benzoyl l-aspartic acid*, m.p. 184°–185° (corr.); has $[a]_D^{20°} +37·4°$, *leucyl aspartic acid* CH_2Pr^β. $CH(NH_2) \cdot CO \cdot NH \cdot C_2H_3(CO_2H)_2, H_2O$ decomposes at 180°–182° (corr.) (Fischer and Koenigs, Ber. 1904, 37, 4585); and the *picryl* derivative $C_{10}H_8O_{10}N_4$ has m.p. 137°; *aspartic diamide* $C_2H_3(NH_2)(CONH_2)_2$, m.p. 131°, has $[a]_D -7°$, and gives the biuret reaction (Fischer and Koenigs, Ber. 1904, 37, 4585). Aspartic acid resembles asparagine in its physiological action (Salkowski, Zeitsch. physiol. Chem. 1904, 42, 1207; Andrlik and Velich, Zeitsch. Zuckerind. Böhn, 1908, 32, 313).

d-Aspartic acid, obtained by hydrolysis of *d*-asparagine (Piutti, Ber. 1886, 19, 1694), or from *l*-bromosuccinic acid and aqueous ammonia at −40°, a Walden rearrangement taking place (Fischer and Raske, Ber. 1907, 40, 1051); is also obtained from a solution of the racemic acid [(d+l) aspartic acid] which has been inoculated with a mould grown on *l*-aspartic acid (Engel, Compt. rend. 1887, 106, 1734). *Benzoyl d-aspartic acid*, obtained by Fischer (Ber. 1899, 32, 2451), by the resolution of the racemic compound, through the brucine salts, has m.p. 181°–182°, $[a]_D^{20°} -37·6°$ in alkaline solution.

Inactive, *(d+l)-aspartic acid*, prepared by the action of boiling hydrochloric or nitric acid on the product obtained by heating the ammonium salts of malic, malc̈ic, or fumaric acids (Dessaigne, Compt. rend. 1850, 30, 324); by heating an aqueous solution of the hydrochloride of *l*-aspartic acid at 170°–180° for some hours (Michael and Wing, Ber. 1884, [1] 2984); by heating *d*- or *l*-aspartic acid with 2 mols. HCl (sp.gr. 1·107) at 170°–180°, or from an aqueous solution of equal parts of the *d*- and *l*- acids; the racemic acid crystallises out (Piutti, Ber. 1886, 19, 1694); by reducing and hydrolysing

the sodium salt of ethyl oximino-oxalacetate (Piutti, Chem. Zentr. 1888, 68). $(d + l)$-Aspartic acid forms small monoclinic prisms; 100 grams of water dissolve y mg. of the acid at $t°$, where

$$y = 517 + 21·693t - 0·165t^2 + 0·0079t^3$$

(Engel, Compt. rend. 1888, 106, 1734). The copper salt $CuC_4H_5O_4N,4\frac{1}{2}H_2O$ is dark-blue (Engel. *l.c.*). The *benzoyl* derivative has m.p. 164°–165° (corr.), and can be resolved into its active components by crystallising the brucine salt (Fischer, Ber. 1899, 32, 2451).

M. A. W.

ASPHALT. *Compact bitumen*, *Mineral pitch*, *Jews' pitch*, *Bitumen of Judæa*. (*Judenpech*, *Erdpech*, *Bergpech*, Ger.; *Goudron minéral*, Fr.) A name given to the solid varieties of bitumen. In its purest form asphalt presents the appearance of a black or brownish-black solid substance, possessing a bright conchoidal fracture. It melts at 100°, burning with a brilliant flame and emitting a bituminous odour. Sp.gr. 1·0–1·68. Asphalt is insoluble in alcohol and water, soluble in about five times its weight of naphtha, and in benzol. It is dissolved by alkalis and alkaline carbonates.

By dry distillation a yellow oil, Asphalt oil, is obtained. It consists of hydrocarbons mixed with a small quantity of oxidised matter. It begins to boil at 90°, but the boiling-point gradually rises to 250°. The portion boiling below 200° has the sp.gr. 0·817 at 15°; that above 200° has a sp.gr. of 0·868 at 15°. Both portions gave by analysis about 87·5 p.c. carbon, 11·6 p.c. hydrogen, and 0·9 p.c. oxygen, which is nearly the composition of oil of amber (Völckel, Annalen, 88, 139). Nitric acid converts it into a resin, having the odour of musk and the taste of bitter almonds.

Boussingault obtained from the asphalt of Bechelbrunn a pale-yellow oil, *petrolene*, having a faint taste and bituminous odour, of sp.gr. 0·891 at 21°, and boiling at 280°.

By heating asphalt to 250° for 48 hours, the volatile oils are driven off; a black solid substance, *asphaltene*, is obtained. It becomes soft and elastic about 300°.

The purest asphalt is found on the shores of the Dead Sea and in the pitch lakes of Trinidad and Mexico. Rocks more or less impregnated with bitumen, to which the name earthy or crude asphalt is given, are found at the Poldice mines, Cornwall; near Matlock, Derbyshire; at Haughmond Hill, Shropshire; at the Hotwells, near Bristol; in the limestone near Glasgow; the freestone near Edinburgh; and generally throughout the Orkneys. Large deposits occur also at Seyssel, Dépt. de l'Ain; at Bechelbrunn and Lobsann, Lower Rhine; at Bastennes and Dax, in the Dépt. des Landes; in the Val de Travers, Neuchatel and other places.

Asphalt is separated from the minerals with which it is associated either by melting the mass, allowing the earthy matters to subside and removing the bitumen; or by boiling with water, which causes the bitumen to run out in the melted state; or by the action of hydrochloric acid, which dissolves the calcium carbonate and leaves the asphalt; or with oil of turpentine, which dissolves out the bitumen. Murrie (J. Soc. Chem. Ind. 3, 182) describes the

methods used in Italy for the extraction of bitumen from crude asphalt.

The Val de Travers asphalt contains about 20 p.c. of bitumen, and it only requires the addition of 6 to 8 p.c. of mineral or coal tar to convert it into a plastic, workable mastic of good quality for pavements and hydraulic works.

The modern method of laying down asphalt pavement is to first prepare a foundation of concrete the surface of which is carefully flattened. On this even surface, when thoroughly dry, the melted asphalt is spread with a wooden trowel, and the surface is finally smoothed over. The liquid Val de Travers, Limmer's, and Barnett's asphalts used for this purpose are all mixed with grit or sand, and so present rougher surfaces than those pavings which consist of asphalt alone. Brande (D. R. P. 4993, 1878) mixes ground slag with the asphalt instead of sand.

Another method of paving is to break up the bituminous ore, and heat the fragments till they crumble to powder. A layer of this hot powder, from 16 to 20 inches thick, is laid on the dry concrete and compressed by stamping with hot irons.

Artificial asphalt, or gas-tar asphalt, is a mixture of chalk, sand, or limestone with the thick, pitchy residue obtained by evaporating the more volatile portions of gas tar. The mineral substance must be heated to expel moisture and adhering air, and then added to the strongly heated pitch.

In addition to the use of asphalt for pavements, water-tight tanks, and coatings for iron tubes used for conveying gas or water, &c., it is used in photography, in photo-lithography, and photo-engraving, owing to the asphalt becoming insoluble in turpentine after exposure to light. In the latter case copper plates are covered with a thin coating of pure asphaltum, or bitumen of Judæa, dissolved in benzene or chloroform. When dry, the plate is exposed behind a film to bright sunlight for half an hour, and then developed by first softening the soluble portion of the asphaltum with olive oil, to which subsequently a little turpentine is added. As soon as the lines are bare the turpentine and oil must be washed away by the action of water.

Methods for preparing asphalt for paving and other purposes are described by Dagusan (D. R. P. 4999, 1878; Dingl. poly. J. 232, 547); Kalilbetzer (D. R. P. 5646, 1878); Zadig and Neuberg (D. R. P. 5678, 1878; Dingl. poly. J. 233, 490); Clark (Eng. Pat. 8036, 1884: J. Soc. Chem. Ind. 5, 183); Kettmann (Eng. Pat. 12425, 1884; J. Soc. Chem. Ind. 4, 675); Richter (Siefenseid Zeit. 23, 272; J. Soc. Chem. Ind. 2, 474).

Native asphalt can be distinguished from artificial asphalt by extracting with carbon disulphide, filtering, evaporating to dryness, and heating the residue till it can be ground to a fine powder; 0·1 gram is treated with 5 c.c. of fuming sulphuric acid for 24 hours, and is then mixed, with continuous stirring, with 10 c.c. of water. If pitch or coal tar be present, the solution will be of a dark-brown or blackish tint; if not, the solution will be of a light-yellow colour (*v.* Pitch).

ASPHODEL. The tuberous roots of *Asphodèle de Sardaigne*, of *Asphodelus ramosus* (Linn.),

and other species of the same genus, contain a fermentable substance from which alcohol may be prepared (*cf.* Rivière and Bailhache, Compt. rend. 1895, 121, 659). By drying and coarsely grinding the tubers, Landerer obtained a powder which, mixed with water, formed a strong glue. Badoil and Lienders obtain tannin from the pulp left after the extraction of the alcohol.

ASPIDIN *v.* Filix-mas.

ASPIDOSAMINE and **ASPIDOSPERMINE** *v.* Vegeto-alkaloids.

ASPIRATORS. Aspirators are used to draw air or other gases through any apparatus connected with them, and were probably first employed by Brunner in his analyses of air, 1830–1840 (Pogg. Ann. 20, 274; 24, 569; 31, 1). The process of aspiration or inhaling of air is, however, most common, being necessary to the life of animals and to the ventilation of buildings, mines, &c., to change the air so that it may support life. In other analyses of air by Dumas and Boussingault, an exhausted globe or jar was used as an aspirator (1841, Ann. Chim. Phys. [3] iii. 257). When a vessel is emptied of liquid, air must enter to take its place, and the common aspirator, in its various forms, is a vessel with two openings, the lower to serve as outlet for the water or liquid, and the upper as inlet for the air or gas to be aspirated. With suitable fittings a siphon may be used instead of the lower opening, or the apparatus may be modified into a bell-jar standing over a basin or large jar, the air being drawn in through the neck of the bell-jar. This is Mohr's aspirator, which is sometimes poised like a gasholder to facilitate filling and emptying of the bell-jar (Mohr, Lehrbuch der Titrirmethode, 1855, Brunswick).

From their introduction, aspirators were used not only to draw in gases through apparatus and reagents employed, at a regulated rate, but also to measure the gases so manipulated by simply measuring or weighing the liquid run out of the aspirator. For approximate readings aspirators of glass may be graduated, and those of metal may be provided with gauge glasses.

Numerous forms of the simple aspirator have been invented by Brunner, Regnault, Mohr, and others. Fig. 1 is perhaps the form in most fre-

Fig. 1.   Fig. 2.

quent use, and is generally of glass, plain or graduated. Fig. 2 is a very convenient form, described by Clemens Winkler (Industrie-Gase, 1877, 39–41) constructed of zinc plate and supported on a wooden tripod. The second tap below, on the side tube, is useful in filling the aspirator with water. Fig. 3 is the form often used in testing the gases from chemical works. It is simply a cubical or rectangular box made

of sheet lead, with a graduated gauge glass, and can be opened at A to fill it with water.

Double aspirators. In short operations the simple aspirator requires no refilling nor special attention after the taps are adjusted. To obviate the inconvenience of stopping to change or refill that would be necessary in longer operations, Brunner, Boisgiraud, Dancer, Muencke, and others have contrived double aspirators so connected that each vessel is alternately above and below, and one or other always ready for use. The aspirating bottles may be mounted on a common axis as in Dancer's swivel aspirator,
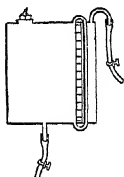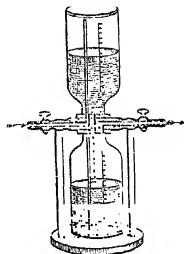
Fig. 3.   Fig. 4.

Fig. 4 (Chem. News, 1864, 10, 295). These swivel aspirators are very convenient, but the difference of water-level in the two bottles is not under the control of the operator and varies between the height of one bottle and a very small minimum.

Figs. 5 and 6 show an arrangement devised
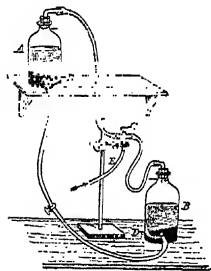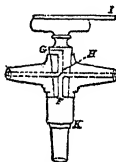
Fig. 5.   Fig. 6.

by the author, which has certain advantages. The bottles A and B are connected as shown, being raised and lowered alternately. The four-way tap C (shown larger in Fig. 6) has its index I turned towards the upper bottle in aspirating and towards the lower bottle in blowing. It is made from a good gas tap by boring up the centre of the plug at F, leading out the hole at G. A small piece of metal H is then fitted and soldered diagonally where the holes cross, a piece of tubing K soldered on to the socket of the tap, and an index I above the plug.

Paraffin wax is used to adjust the bottles for exact measurement, and to obtain a fine adjustment below at D, as well as above, by a mark on the neck of the bottle. The proper quantity of melted wax is run through a wide tube into the warm bottle slightly tilted. A passage from the

tubulure to D at the side of the bottle is secured by pushing an indiarubber tube through the tubulure and fixing it in the proper position before the wax is run in, and after the wax is quite solid this tube is drawn out. The passage should be curved, so that on emptying the bottle of water the water runs out to the mark at D. The bottles are then adjusted by weighing their content of water between the marks and adding or removing paraffin till at the standard temperature and pressure they hold the exact quantity of water corresponding to the volume required. In successive weighings of bottles so adjusted the differences should not exceed 0·1 gram. To avoid loosening of the wax from direct contact with the glass, the bottles should be preserved from changes of temperature and from mechanical vibration, &c.

Constant or automatic aspirators. Instruments of this class have been invented by Guthrie (Phil. Mag. [4] 15, 64) and by Bonny (Winkler's Technical Gas Analysis, trans. by Lunge, 17). In each of them a pipe from the water supply leads a constant stream of water into a vessel, which, when full, is emptied by a siphon, whose tube is of larger size than the supply pipe. The arrangement thus acts on the principle of the intermittent siphon, and the vessel is filled and emptied at regular intervals. In Bonny's instrument these are registered by a simple mechanism, and the total volume passed is known on measuring the volume passed in one operation.

The Sprengel and injector pumps may be used as constant aspirators (*v.* FILTER PUMPS). By means of a collecting box attached below the pumps to allow the gas and water to escape at different levels, the gas may be measured by passing it through a small gas meter (Davis, J. Soc. Chem. Ind. 211).

J. Grossman (Winkler's Industrie-Gase, 218) has invented a small mercurial aspirator, on the principle of the Geissler pump, with two reservoirs, which are alternately raised and lowered. It is fitted with registering apparatus.

In testing air and gases from confined places, works, &c., Angus Smith, Davis, and others have used small pear-shaped aspirators of indiarubber. These are emptied by simply squeezing in the hand. The air escapes by a valve, of which the simplest is a small slit in the rubber connecting tube, opening outwards like a Bunsen's valve. The rubber recovering its form draws a certain volume of gas through the testing apparatus, and it is easy to ascertain approximately the total volume of gas corresponding to any given number of times the aspirator has been filled. Another larger aspirator of this class is of bellows form, like a concertina, the folding part being of indiarubber. This aspirator is frequently used for filling by displacement jars or bottles with gas to be tested. The common single-barrel air pump or apparatus, on the same principle, is also applied in this manner as an aspirator.

At the British Association Belfast meeting, 1874, the late Prof. Andrews showed how an ordinary wet gas meter could be converted into an aspirator by applying motive power to the hollow axis of the drum, thereby causing it to suck in air at the inlet side and at the same time to measure the air on the meter index. Using

mercury as liquid in a cast-iron meter, a similar arrangement forms the basis of the Barr and Stroud air pump applied in the evacuation of bulbs for electric lighting lamps (J. Soc. Chem. Ind. 1896, 640 ; Eng. Pat. 13188, July, 1895).

<div style="text-align:right">T. F.</div>

ASPIRIN. Trade name for acetyl salicylic acid $C_6H_4(COOH)O \cdot CO \cdot CH_3$, used as an anti-rheumatic.

ASSAYING. Assaying, ' the trial of metals,' a term originally applied only to the testing of gold and silver, is now usually extended to the determination of the quantity of the valuable metal in an ore or metallurgical product. It is also sometimes taken to include the estimation of any element which may prejudicially affect the value of the ore, but it is more usual to discuss this together with such work as the complete analysis of ores, slags, furnace materials, fuel, &c., under the heading of ' metallurgical analysis.' A brief account of some of these sections is given below.

The art of assaying is of great antiquity. The use of the touchstone for testing gold in India was referred to by Mathuranatha (Hist. of Hindu Chemistry, by Ray, ii. 231), and was probably known in the Greek world at least as early as B.C. 700, when the first electrum or gold-silver coins were manufactured. At any rate the touchstone found its way into Greek mythology. The testing of gold alloys by cementation was described by Pliny, by Strabo, and in the eighth century A.D. by the Arabian Geber, who was also familiar with the method of cupellation, and is reputed to have discovered nitric acid. The parting assay of gold with the aid of this acid is referred to in a decree of Philippe de Valois in the year 1343, confirming its use in the French Mint. Alloys of silver with copper were tested by observing the degree of blackening caused by heat in the Roman Mint under the Republic (Rochon, Essais sur les Monnoies, 17, 1792).

It is probable that ores were not valued except by inspection until the Middle Ages. The first clear references to ore-assaying are to be found in the writings of Biringuccio, Agricola, and Ercker in the sixteenth century, but the art was evidently regarded by these authors as already ancient at the time at which they wrote. Ercker, writing at Frankfort in 1580, describes the fire-assays not only of several different kinds of gold and silver ores, but also of the ores of copper, lead, tin, antimony, iron, mercury, and bismuth. Assaying by means of ' wet methods,' volumetric, gravimetric, and electrolytic, is of comparatively recent introduction (excepting the parting assay of gold), but has now in great part superseded the ancient processes involving the use of furnaces.

Sampling.—Whether the material to be assayed is a portion of a vein underground, a heap of broken ore, pigs of metal, or a delicate piece of jewellery, in every case a representative sample must be obtained. In the case of ore *in situ* underground, pieces are taken from a number of different points and either mixed or examined separately. Ore which can be moved is reduced in bulk either by hand or by machinery, and is generally crushed finer between each successive reduction in bulk. Every second, fifth, tenth, or twentieth shovelful or car-load

may be set aside as a sample, or the whole heap may be made into a perfect cone, which is flattened and divided into four quarters along two diameters. Two opposite quarters are removed and mixed, and the process of ' coning and quartering ' repeated as often as necessary. A heap or vat of ore or tailings, which must be sampled without being moved, is pierced at regularly spaced intervals by a sampling tube which resembles a cheese-taster, and withdraws a cylindrical sample extending to the bottom of the vat or heap.

In automatic sampling machines, which are much used in Western America, the crushed ore is made to slide down an inclined plane or rotating cone, and a portion of the stream of ore is deflected and set aside as a sample. Those machines are preferred which momentarily take the whole stream of ore at regular intervals of time. Further reduction in the laboratory is effected by coning and quartering or by a machine such as the *riffle* or *sampling tin*, which consists of a series of metal troughs arranged side by side and fastened at equal distances from each other. A stream of ore let fall on it is in part retained by the troughs and in part passes through.

The final grinding of the ore is effected by means of an iron pestle and mortar, or of a large hammer with a curved face sliding on an iron plate (or *buckboard*), or by some form of rolling or grinding mill. The crushed ore is passed through a sieve, the fineness of which varies according to the ore and the method of assay. If a panning test is required, a 20-mesh sieve (*i.e.* one with 20 holes to the linear inch) suffices. For most fusions, *e.g.* dry lead assay, a 60-mesh sieve is used. Gold ores are crushed through an 80- or 100-mesh sieve, and in the case of telluride ores of gold, the best results are obtained by using 120-mesh sieves. Before it can be passed through a fine sieve, the ore must be dried, so that the *moisture* is determined on coarsely crushed ore by drying at 100° on a water-bath, or, if the dry material is not likely to be affected in any way by a somewhat higher temperature, it is heated on a sand-bath. In crushing rich gold and silver ores, mint sweepings, &c., pieces of metal are found which become flattened out and are caught on the sieve. These ' metallics ' are treated separately, and the value calculated on the weight of ore from which they were derived.

The dried and crushed sample is thoroughly mixed by means of a spatula in a basin, or on rubber-cloth, before the portion required for assay is weighed out. If stored in a bottle or tin, the movement of the vessel causes the heavy particles to settle, so that the material at the bottom becomes richer than that at the top.

Ingots of metal are sampled by cuts taken from the corners or edges, as in the case of refined gold and silver, or by drillings from a number of different spots, as is sometimes done in the case of iron and steel. Pigs of argentiferous lead are sometimes sampled by drillings or saw cuts. Base gold and silver ingots, and in many cases ingots of steel and pigs of lead, are melted and stirred, and a portion dipped out and granulated by pouring into water, or cast into a little ingot. Coins are sampled in various ways, silver coins being seldom uniform

in composition. The simplest method applicable to all is to roll them out and cut them into a large number of little pieces, so that all parts of the coin may be represented in the portion taken for assay. This method is adopted in the Philadelphia Mint, but is not in general use, other more complicated methods being preferred. Gold and silver wares are usually pickled, and are richer on the surface than in the interior. In sampling them, it is accordingly necessary to remove the outside by scraping and then to scrape off a portion of metal for assay.

The *preliminary examination* of ores includes careful inspection, which is all the more useful if some comparatively large pieces are included in the sample. The proximate constituents, such as quartz, pyrites, magnetite, galena, &c., are thus observed, and the proportions in which they are present roughly estimated, this information being required in making-up furnace charges. Frequently a concentration test is made in a miner's pan (a flat-bottomed sheet-iron pan about 20 inches in diameter, and 3 or 4 inches deep, with sloping slides) or a vanning shovel, or in any basin, pan, or even clock-glass available. For this purpose a portion of 25 grams or more is weighed out, stirred and shaken with water by a circular motion on the shovel, and the lighter particles rinsed away and caught in a basin. Finally by a combination of the circular motion, and a series of jerks, the denser particles are thrown up and the lighter ones washed down the shovel. The concentrates are examined with a lens or separated, dried, and weighed, or treated with acid, or examined by means of the blowpipe, or in other ways, in order to determine the presence or absence of elements likely to interfere with the method of assay chosen. The vanning shovel is used particularly with tin ores, but may be applied to any others. Panning tests are especially useful in the examination of gold ores, but are also required to determine the nature of the 'mineral' or compounds of the heavy metals in almost all ores. The test may be applied to half a gram of ore in a watch-glass, if no more can be spared.

The furnaces used by assayers are the muffle furnace, and the melting or wind-furnace.
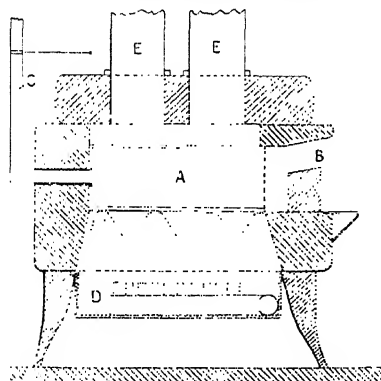
FIG. 1.

The *muffle furnace* consists of a small oven or muffle of refractory fireclay open at the front, and having an arched top. It is heated by coal, coke, oil, gas, or electricity. Muffles vary in size according to the amount of work to be done, but those used at the Royal Mint may be considered full size. Sectional views of one of these furnaces are shown in Figs. 1 and 2. The muffle A is $14\frac{1}{2}$ inches long, $8\frac{1}{4}$ inches wide, and 5 inches high, inside measurements, with walls about $\frac{3}{8}$ inch thick. The mouth is closed by the firebrick B and by a sliding plate. Air enters through holes in the sliding plate and passes out at the back through the tube c,
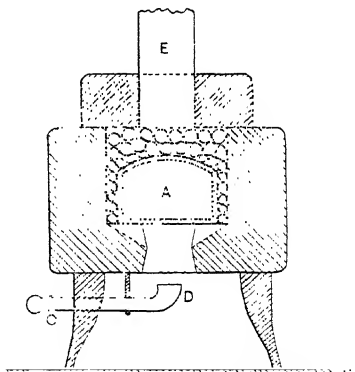
FIG. 2.

which has a sliding damper and leads into the main flue. The fuel is ordinary gas, supplied by a row of bunsen burners D, and complete combustion of the gas may be aided by clay fireballs surrounding the muffle. The flues E E carry off the waste gases. The furnace walls consist of firebrick bound with iron and covered with a thick layer of magnesia and asbestos to check radiation. No chimney stack or forced draught is required for this furnace.

A *melting furnace* adapted for the use of coke as fuel and suitable to make fusions in assay operations, is shown in section in Fig. 3, in which A is the fireplace, B the flue, C the ashpit, D the damper, and E the firedoor. The most useful size of the fireplace is about 9 inches square, and about 10 inches in depth from the firebars to the flue. The furnace is built of brick and lined with firebrick. It is bound with angle iron or covered with iron plates bolted together and furnished with tie rods. Gas-melting furnaces with natural draught
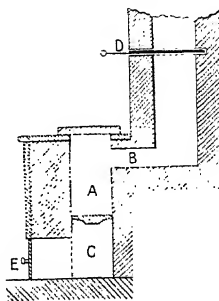
FIG. 3.

or using a blast of air are less common. The fluxing crucibles (a, Fig. 4) consist of fireclay or a mixture of plumbago and fireclay, or, in the assay of galena, of wrought iron. They are of different sizes and shapes, the best-known being the Battersea (round, Cornish, and triangle), French, Hessian, and Colorado cru-
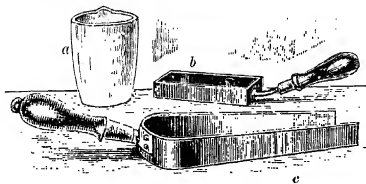
FIG. 4.

cibles, the last-named being used for making fusions in the muffle, a common practice in America. Most crucibles require careful anneal-ing before being used. Roasting dishes made of fireclay (a, Fig. 5) are for the roasting of ores ; scorifiers (c) are used in the process of scorifica-
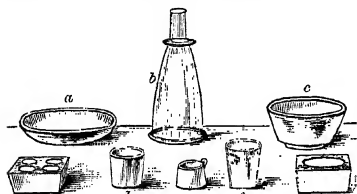
FIG. 5.

tion ; cupels of various shapes and sizes (d, e) are made of compressed bone-ash or magnesia, and are required in the assay of the precious metals. The bone-ash cupels may be made by the assayer, and must be carefully dried before use. Magnesia cupels are usually bought ready-made. A parting flask is shown in
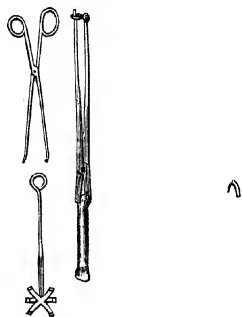
FIG. 6.

b, Fig. 5. The furnace implements (Fig. 6) consist of basket or circular tongs for lifting crucibles out of the furnace, pouring tongs,

cupel tongs, scorifier tongs, and button tongs, with various scrapers, pokers, &c. Iron slag-moulds (b, Fig. 4) are required for casting the results of scorifications and of fusion assays, and hammers, anvils, slag hoops, and other implements are also required. The charging scoop (c, Fig. 4) is required for charging metal, &c., into red-hot crucibles.

The *reagents* used in fire assay may be classed as fluxes, agents for reducing, oxidising, sulphurising, and desulphurising, and covers to protect the contents of the crucible from the action of the air, furnace gases, &c. Generally speaking, an ore consists of compounds of a heavy metal or metals (the mineral), together with a quantity of earthy materials, such as quartz, silicates, &c. (the gangue). It is re-quired to reduce the valuable constituent to metallic form, and to incorporate the remainder of the ore in a fusible slag, through which the particles of metal may settle to the bottom, where they collect in the form of a button. Sometimes a regulus or matte (sulphide of a heavy metal) or a speise (arsenide of a heavy metal) forms a separate layer between the metal and the slag, and a cover, say, of common salt, may be provided which is lighter than silicate slags and floats on the top. On breaking open a cold crucible in which a fusion has been made, there are, therefore, frequently four layers.

The principal fluxes used are sodium car-bonate, which forms fusible mixtures with acid (siliceous) ores, and also acts as a desulphuriser, converting pyrites into a mixture of sulphides of iron and sodium which does not form a regulus, but is dispersed through the slag. Carbonate of soda is generally used in the form of powdered bicarbonate, which gives up half its carbonic acid without fusion. Soda crystals give up their water of crystallisation with ebullition, and are not suitable unless previously dried. Basic ores require borax, which forms fusible mixtures with oxides of iron, lime, &c. ; and increases the fluidity of most charges. Crystallised borax powder on heating swells up enormously, gives up its water and fuses into a glass. The swelling may occasion loss in the assay if the crucible is too full. To avoid this, borax glass may be used, which is equivalent to about double its weight of ordinary borax. Litharge is a useful flux, especially for oxides of iron, copper, &c., but attacks and corrodes the crucibles. Fluor-spar is sometimes used, especially for phosphates. Sand is often required to protect the crucible from attack by basic ores.

The reducing agents are carbon (charcoal powder or lampblack), flour, tartar or argol (crude hydrogen potassium tartrate), and occasionally potassium cyanide. One part of charcoal is about equal to two parts of flour or five of tartar, but tartar also acts as a flux, being converted by heat into carbon and potassium carbonate. Black flux is a reducing mixture made by deflagrating one part of nitre with two and a half parts of argol.

The chief oxidising agents, which are also desulphurisers, are hot air, litharge or red lead, and nitre. Iron is often used as a desulphurising agent. The ordinary materials used as covers are borax and common salt.

The *balances and weights* do not differ, as a rule, from those used in ordinary chemical

analysis, the most notable exception being in the case of those used in the assay of gold and silver. The proportion of these metals present in ores is reported in troy ounces, pennyweights, and grains per ton, or sometimes in ounces and decimals or in pennyweights and decimals. The weight of ore taken for assay accordingly contains as many milligrams as there are ounces troy in a ton (29,166 in a ton of 2000 lbs., and 32,666 in a ton of 2240 lbs.). This weight of 29·166 grams is called an *assay-ton* (or A.T.), and boxes of weights made up of assay-tons and decimals are used by many assayers. Then the gold extracted from the sample of ore is weighed in milligrams, and can be reported without calculation. In the assay of gold bullion the weights commonly range from '1000' downwards, where 1000=0·5 gram or some other unit such as 5 grains. Much tedious calculation is avoided by thus marking the weights so that their face-value gives at once the result of the assay. Again, in assaying silver by precipitation as chloride (India Mint method, see p. 327), since 18·815 grains of pure silver are contained in 25 grains of chloride, it follows that if 18·815 grains of an alloy be always taken for assay, and the resulting chloride be weighed out with a series of weights the largest of which is marked 1000, and is equal to 25 grains, and the others are marked correspondingly, then the subsidiary weights of this series will indicate the result of the assay without calculation. A similar series can, of course, be arranged for any special purpose.

The balances used for weighing gold and silver in bullion assays are light and delicate, taking about 2 grams as their maximum of weight, and turning to one hundredth of a milligram. Usually, one division of the ivory scale is made equal to 0·05 mg. Balances for weighing the parted gold in ore assays are still more delicate. The maximum weight which they can carry is only 1 gram or even less, and they turn with one-hundredth or in some cases only one five-hundredth of a milligram. Milligram and half-milligram riders are used, but the final reading is always based on the deflection from the zero position of the pointer, measured by the number of divisions on the ivory scale covered by the swing. At the present day short beams of 6 inches, 4 inches, and even 8 cm. in length, are in use, so that the balances are very rapid in action in spite of their sensitiveness.

In quantitative blowpipe work on gold and silver, it has been found possible to dispense altogether with a delicate balance, and to use an ivory scale (Plattner's scale), by which the diameter of the bead of metal is accurately measured. The principle has been extended in the assay of poor materials, and beads of microscopic dimensions are placed on the stage of a microscope and measured by means of a micrometer eyepiece. In this way L. Wagoner (Trans. Am. Inst. Mining Eng. xxxi. 1901, 798) obtained a close approximation to the weight of beads of silver of 0·02 mm. in diameter, which weighed about 0·00004 mg.

The above summary has special reference to the requirements of a laboratory for making dry or fire assays. For wet assays, the apparatus and reagents are those of the ordinary analytical laboratory (*v.* ANALYSIS).

In all methods of assaying, wet or dry, time must be considered as well as accuracy. It is sometimes important to arrive at a result in the course of an hour or less, and some of the methods described are intended for such emergencies, when extreme accuracy must be sacrificed. It is also necessary to observe that assay methods are intended to be comparative, and wherever it is possible check assays on similar materials of known composition should be made side by side with the assays of ores or other bodies requiring examination, and a correction applied to the results. In the following pages, only methods in common use in assay offices are described. The methods of ordinary analysis are generally omitted or made the subject of brief reference.

Aluminium. There are no special methods of assaying the ores of this metal. The silicates are broken up, and the silica removed as usual (see p. 329), and the acid solution of the bases is treated so as to separate the metals contained in it. Aluminium is precipitated and weighed as phosphate $AlPO_4$, or oxide Al_2O_3. It is sometimes weighed as oxide together with oxide of iron Fe_2O_3, and also P_2O_5, if these constituents are present in the ore. The last mentioned constituent is of course combined as phosphate. The phosphorus and iron are then determined, aluminium being estimated by difference (Low's Technical Methods of Ore Analysis, 1st ed. 22).

Antimony. The antimony in ores may be determined by fusion with cyanide of potassium or with iron (avoiding excess) and black flux, but the results are unsatisfactory. The sulphide of antimony in an ore may also be approximately determined by charging 500 grams of ore broken to nut-size into a clay crucible with a perforated bottom. This crucible is fitted into another of about the same size, and the joint carefully luted. A cover is also luted on, and the whole is slowly raised to a red heat. The sulphide of antimony fuses and liquates into the lower crucible, from which it can be detached when cold, and weighed. The fused sulphide of antimony, if pure, contains 71·7 p.c. of the metal. The valuation of antimony sulphide ores is usually effected, according to Bedford McNeill (Berenger's Assaying, 11th ed. 226), by having recourse to the ordinary smelting operation, which is to be used in treating the ore on the large scale. Charges of about 20 kilos. of ore are used for the valuation.

The wet methods of estimation of antimony in ore are far more accurate than those referred to above. The ore is fused with sulphur and sodium carbonate, and then digested with water. A solution of an alkaline sulphocompound of antimony is thus obtained, from which a mixture of antimony and arsenic sulphides and free sulphur is precipitated by the addition of dilute hydrochloric acid. After the arsenic has been separated, the antimony sulphide is weighed or is oxidised by fuming nitric acid, and weighed as Sb_2O_4. Ores may also be attacked by hydrochloric acid. The antimony in the separated sulphide may be estimated volumetrically, dissolving the sulphides in hydrochloric acid and chlorate of potash, warming to expel the chlorine, adding an excess of potassium iodide, and titrating

with thiosulphate of soda (J. Soc. Chem. Ind. xv. 255).

Arsenic. The determination of arsenic in ores and metallurgical products is usually made by Pearce's method, which consists in fusing about 0·5 gram of the ore with 5 grams of a mixture of equal parts of sodium carbonate and nitre, dissolving out the soluble arsenates of the alkalis and precipitating the arsenic in a neutral solution by means of silver nitrate. The precipitated brick-red silver arsenate Ag_3AsO_4 is filtered off, dissolved in nitric acid, and the silver in it determined by Volhard's thiocyanate method. The amount of arsenic present can then be calculated (Low's Ore Analysis, 41). Small quantities of arsenic in metals and minerals may be separated by distillation with ferric chloride and calcium chloride in a hydrochloric acid solution, the distilled arsenious chloride being condensed in a vessel of cold water (Berenger's Assaying, 384). (For arsenic in steel, *see* p. 325.)

Bismuth, if present in an ore in the metallic state, may be determined by liquation, the method of procedure being similar to that used in liquating sulphide of antimony (*q.v.*). The bismuth in an ore may also be determined by fusing it with fusion mixture, common salt, and cyanide of potassium. These methods are inexact, and bismuth is usually determined by being weighed as Bi_2O_3 after precipitation as carbonate, or as BiOCl on a weighed filter or a Gooch crucible after being dried at 100°. Bismuth in metallic lead is precipitated and weighed as BiOCl, and in metallic copper it is detected by the colour given to lead iodide. (For estimation of bismuth in copper, *see* p. 322.)

Chromium occurs in chrome-iron ore and sometimes in other iron ores, in pig-iron and in steel. Small quantities of chromium in iron ores, after separation from other metals and earths, are precipitated by lead acetate in an acetic acid solution, and weighed as $PbCrO_4$, or, in the alternative, reduced by sulphurous acid and the chromium precipitated from the green solution by means of ammonia and weighed as Cr_2O_3. Chrome-iron ore is assayed by a volumetric method based on the oxidation of ferrous iron by chromium in the form of chromate. The chromium is oxidised by peroxide of sodium (J. Iron and Steel Inst. xlviii. 153). The ferrous iron is added in the form of a weighed amount of ferrous ammonium sulphate or of a weighed amount of metallic iron dissolved in sulphuric acid. The excess of ferrous iron present in the solution containing the chromium is titrated with permanganate. Chromium in steel is precipitated and weighed as chromium phosphate (Chem. News, lvii. 1888, 153), or as chromic oxide Cr_2O_3.

Cobalt. (*See* **Nickel,** p. 326.)

Copper. The principal ores of copper are (*a*) native copper; (*b*) sulphide ores, copper pyrites or yellow ore, erubescite or purple ore, grey copper ore, &c. : (*c*) oxidised ores, malachite, silicate of copper, &c. The treatment of copper ores results in the production of copper matte or regulus containing from 30 to 50 p.c. of copper, and cement copper or copper precipitate, containing 70 p.c. or more of metallic copper. In addition to these materials, ordinary commercial standard copper, refined copper, and the alloys of copper require to be assayed.

The chief methods in use are as follows :—

(1) *Dry or Cornish assay*, long used in connection with the sale of copper ores, but applicable chiefly to mattes and rich sulphide ores. It is especially unsatisfactory when dealing with poor ores, but gives low results in all cases, the loss, according to Beringer, ranging from 2 p.c. of the copper present in the richest materials to 33 p.c. of the copper in 2 p.c. ore. It consists in fusing the calcined regulus for metallic copper and refining the copper. Rich oxidised ores are fused for metal at once. The amount of ore taken for assay is 400 grains, but with rich material only 200 grains or even 100 grains are taken. The fluxes vary with the nature of the ore, in which there may be too much sulphur and iron, as in copper pyrites, &c., or too little, as in grey copper. The following are examples of the charges :—

Ore			200 grains		100
Nitre	.	.	50	,,	—
Lime	.	.	200	,,	200
Fluorspar	.	.	200	,,	200
Glass	.	.	150	,,	150
Borax	.	.	150	,,	150
Hæmatite	.	.	—	.	15–20
Sulphur	.	.	—	.	25–30
Argol	.	.	—	.	30

The charge is fused in a 'large copper' crucible at a low red heat, which is gradually raised. After about 15 minutes the charge is poured into a conical mould, and, as soon as the slag is solid, it is taken up by tongs, dipped into water, and allowed to dry. When treated in this way, the slag breaks up readily. The regulus is detached by a hammer and crushed to powder in an iron mortar. It should be reddish-brown in colour and contain about 50 p.c. of copper and 20 p.c. of iron. It is roasted in a Cornish crucible in the melting furnace or in a roasting dish in the muffle, at a low but increasing temperature, with continuous stirring at first. When 'sweet,' *i.e.* not smelling of sulphur, at a full red heat, it is mixed with a little charcoal powder, and re-roasted to decompose sulphates. It is then crushed again, if necessary, and fused in the same crucible with argol, borax, and sodium carbonate. A high temperature is required, and the charge is poured in about 15 minutes. The slag is detached and cleaned by a second fusion with more argol and sodium carbonate. The 'coarse copper' obtained in this way is refined by being charged into a very hot crucible and melted. The impurities are oxidised by the air and form a ring of oxides round an eye of copper. Then refining flux, which consists of a deflagrated mixture of nitre, argol, and common salt, is added, and 2 minutes later the copper is poured, and if it is found to be at 'tough pitch,' it is weighed. The slag contains copper, and must be cleaned. (For full details of the method, *see* Percy's Metallurgy, i. 1861, 454–478.)

(2) *Electrolytic assay of copper.* The weight of ore taken for assay depends on its richness, a convenient amount of metallic copper for electro-deposition being from 0·1 to 0·5 gram. When using this method or any of the other

wet methods, the copper must first be brought into solution and usually separated from other metals. Oxidised ores may require merely to be treated with hydrochloric acid. Sulphide ores, mattes, copper precipitate, &c., are attacked by nitric acid, evaporated to dryness, and taken up by hydrochloric acid. Copper slags are fused with sodium and potassium carbonate (fusion mixture), and a little nitre, and are then digested with water and hydrochloric acid. The copper is precipitated from its hydrochloric acid solution by means of sulphuretted hydrogen or (after evaporation with sulphuric acid) by sodium thiosulphate, and the sulphides are filtered off and redissolved in nitric acid. For the electrolytic assay, the solution obtained in this way is diluted, warmed, and filtered into a 200 c.c. flask, and made up to about 100 c.c., of which from 2·5 to 5 p.c. should be nitric acid. Platinum electrodes (spiral and weighed cone or cylinder) are then placed in position, and a current from two Daniell cells in series is passed through for 16 or 17 hours. The cylinder is removed from the colourless solution, washed with water and afterwards with alcohol, dried in a water-oven, and weighed. The copper precipitate should be salmon-red in colour. The solution still contains a little copper, which is estimated colorimetrically, ammonia being added, and the colour, after filtration, compared with those of standard solutions containing known amounts of copper. Silver, mercury, bismuth, arsenic, and antimony interfere with the process, being deposited with the copper. Mercury, however, is separated on dissolving the sulphides in nitric acid. Bismuth turns the copper dark grey, but is not deposited until most of the copper has been thrown down. Arsenic and antimony darken the copper deposit, but may be driven off by heating to dull redness. Lead makes its appearance at the anode. The electrolytic assay is suitable for all materials containing copper (*cf.* ELECTROLYTIC ANALYSIS).

By rapidly rotating the cathode a coherent deposit can be obtained even when a strong current of 10 to 12 amperes per 100 sq. cms. of cathodic area instead of the usual current of 0·5 to 1·0 ampere is used. The time required for the deposition of the copper may thus be shortened to a few minutes (Amer. J. Sci. 1903, xvii. 320, xviii. 56; J. Amer. Chem. Soc. xxv. 896; Chem. Soc. Trans. xci. 373).

(3) *The volumetric assay of copper.* There are two main processes—the potassium cyanide and the iodide methods. Both are in wide use in the assay of ores, alloys, &c. In preparing to use these methods, the copper is brought into solution, and may be separated from other metals, &c., as already described, with any further precautions necessary to remove special impurities. With ordinary pyritic ores, however, containing no zinc, silver, nickel, or cobalt, it is sufficient, in preparing for the cyanide process, to heat the ore gently with concentrated nitric acid to which a little sulphuric acid has been added. It is then diluted, an excess of ammonia or of Na_2CO_3 added, the bulk made up to some convenient amount such as 300 c.c., and the solution titrated with potassium cyanide. The blue solution is decolourised, and when overdone changes to a

straw-yellow colour. The results are affected by time, temperature, degree of dilution, and by the amounts of ammonia and of ammonium salts. The conditions of the check assays on pure copper and those on ores, &c., must therefore be identical, and ferric hydrate, for example, must be present either in both or in neither. The standard cyanide solution, which decomposes somewhat rapidly, contains about 42 grams KCy to the litre, and 100 c.c. of this is equivalent to 1 gram of copper. The reaction, according to Beringer, is represented by the equation:

$$CuSO_4 + 4KCy = 2KCy.CuCy_2 + K_2SO_4.$$
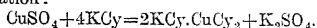
The quantity of copper usually present in an assay is about 0·5 gram. At the finish the effect of an addition of 0·5 c.c. of cyanide is readily observable. Zinc, silver, nickel, and cobalt interfere with the assay, and must be removed before titration.

In the iodide method, the alloy or the sulphide of copper separated from the ore is dissolved in nitric acid, evaporated almost to dryness in order to expel nitrous fumes, and diluted. The solution is then filtered if necessary, and carefully neutralised with sodium carbonate, avoiding excess. One c.c. of acetic acid is then added, which should be enough to redissolve the precipitated copper. Next, after cooling the flask, an amount of about 5 grams of potassium iodide crystals is added (or not less than ten times the weight of the copper present); the solution is diluted to a fixed amount, say 50 c.c.; and the liberated iodine is at once titrated with a solution containing 39·18 grams sodium thiosulphate (equivalent to 10 grams of copper) to the litre. The reactions are represented by the equations:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2I + 2K_2SO_4.$$
$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$
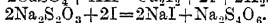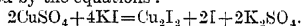
When the yellow colour is almost discharged, 2 c.c. of fresh starch solution is added, and the addition of the thiosulphate continued drop by drop until the blue colour disappears and does not return within 2 or 3 minutes. The effect of one drop or 0·05 c.c. of standard solution, equivalent to 0·5 mg. copper, is observable. The solution is standardised with pure electrolytic copper. Ferric acetate, arsenic, lead, and large quantities of sodium acetate may interfere with the titration. According to J. W. Westmoreland (Beringer's Assaying, 441), sodium acetate counteracts the interference of arsenic and bismuth, and the bad effect of large quantities of sodium acetate is removed by doubling the amount of potassium iodide added. Iron, if present, is precipitated by ammonium phosphate (J. Soc. Chem. Ind. v. 48). Instead of neutralising with sodium carbonate and acidifying with acetic acid, an addition of 20 c.c. of a saturated solution of zinc acetate may be made (A. H. Low).

The colorimetric method of assaying copper is sometimes used in the case of very poor ores, or generally whenever the quantity of copper present is small. Reference has been made to it above.

Examination of commercial copper. Electrolytic and Lake copper are generally nearly pure, but some of the metal sold contains as much as 2 or 3 p.c. of impurities. The most important of these are arsenic, nickel, oxygen, and

Y

phosphorus; but antimony, bismuth, cobalt, gold, iron, selenium, silver, sulphur, and tellurium may also be present. The impurities to be looked for in copper which has passed a high conductivity test are mainly bismuth, selenium, and tellurium. Arsenic and phosphorus are separated as iron arsenate and phosphate mixed with acetate. Gold and antimony are separated by dissolving the copper in nitric acid, and silver is precipitated as chloride or bromide from a nitric acid solution. It may be collected in a precipitate of lead sulphate. Nickel is left in solution by precipitating copper electrolytically, or by sulphuretted hydrogen in an acid solution. Lead is detected by the blackening of the anode in the electrolytic assay, and is estimated as sulphate or chromate.

Oxygen is usually taken by difference, but is sometimes estimated by colorimetric determination of the quantity of the insoluble basic salt of copper formed by the reaction of silver nitrate with cuprous oxide (Hampe's method, Zeitsch. anal. Chem. xiii. 188). The equation representing the reaction is as follows :—

$$3Cu_2O + 6AgNO_3 + 3H_2O$$
$$= 2Cu_2H_3O_3NO_3 + 2Cu(NO_3)_2 + 6Ag.$$
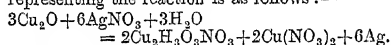
The metallic copper is completely dissolved by the silver nitrate with separation of metallic silver. Bismuth is separated, according to Beringer, by precipitation by sodium bicarbonate. After redissolving in sulphuric acid, it is boiled with sulphurous acid and potassium iodide, and the bismuth in the yellow solution estimated colorimetrically. Tellurium and selenium (J. Amer. Chem. Soc. xvii. 280) are precipitated as iron tellurite and selenite by additions of iron nitrate and ammonia. The precipitate is redissolved in HCl, tartaric acid and potash added, and a current of sulphuretted hydrogen passed. The selenium and tellurium are subsequently precipitated by a current of sulphurous acid in a hydrochloric solution, and parted by boiling with potassium cyanide.

Gold. Gold is generally in the metallic state in its ores, either in the form of grains, scales, pellets, &c., in loose alluvial gravels, or in various forms embedded in quartz or other gangue in veins. It is frequently associated with iron pyrites, blende, &c., but the only native compounds are the tellurides. Besides these, the auriferous materials to be assayed comprise tailings or residues of ores after treatment, copper bottoms, pig lead, unrefined bullion, which contains silver, copper, and other metals, fine (*i.e.* refined) gold, and the commercial alloys used for coinage, plate, &c. The assay of gold ores and alloys is made with greater exactness than other assays, owing to the high value of the metal.

A *panning assay*, or concentration test is carried out as described on p. 317. The concentrates consist of 'black sand' or oxides of iron, titanium, &c., sulphides and arsenides, and sometimes grains of platinum. Free gold is sometimes visible, and is collected by grinding in a mortar with mercury, panning out the amalgam, and recovering the gold by distilling off the mercury or dissolving it in nitric acid. In either case the gold must be parted from the silver as described on p. 323. The panning assay of alluvial gold deposits is usually reported in grains of fine gold per cubic yard, which

weighs about 3000 lbs., or 1½ short tons. In the panning assay, from 60 to 90 p.c. of the gold in the ore is usually recovered.

Ordinary gold ores are assayed by (1) the fusion or crucible method, or (2) the scorification method. In the *crucible assay*, the ore, crushed through an 80-mesh or finer sieve, is mixed with litharge or red lead, charcoal, or argol, and the necessary fluxes, and, fused in the melting furnace or, as in Western America, in the tin affir. The amount of ore taken is usually 1 A.T. (assay-ton, see p. 319), but is sometimes only ½ A.T., and, in the case of poor tailings in which there are only a few grains of gold per ton, as much as 12 A.T. is taken and fused in several charges, the gold being finally collected into one lead button. The fluxes vary with the nature of the ore. The following are typical charges subject to very large variations to meet special cases :—

	A. Silicious ore (grey or white with a little pyrites, &c.)	B. Basic oxidised ore (red or brown)	C. Pyritic ore
Ore . .	1 A.T.	1 A.T.	1 A.T.
Litharge or red lead	1 ,,		1 ,,
Charcoal .	1·2–1·5 grams	2·0 grams	0–1 gram
Sodium carbonate	1¼ A.T.	25 ,,	1 A.T.
Borax .	5–10 grams	10 ,,	10 grams

Sand is added to B and C if necessary for the protection of the crucible from corrosion. The borax is usually not mixed with the charge, but is added as a cover or charged in after the fusion has begun. The charge is well mixed and put into a cold crucible, which it must not make more than two-thirds full, and pieces of hoop iron or two or three tenpenny nails are embedded in the mixture. The crucible is gradually heated, a red heat beginning to appear after about 10 minutes, and a dull red heat not being attained for 30 minutes or more. Tranquil fusion results in 40 or 50 minutes from the time of charging in. The pot is then lifted out of the furnace, the nails removed, and the charge poured into a conical mould or allowed to cool in the pot, which is afterwards broken. When cool, the lead button is detached from the slag by hammering. The button should weigh at least 25 grams. If less than this amount of lead is reduced, a fresh charge is made up containing more charcoal, and any change is made in the fluxes which may seem desirable from the appearance of the slag. If the lead is hard or brittle, owing to the presence of impurities, it is usually scorified, sometimes with the addition of fresh lead, before being cupelled, as otherwise the loss of gold is increased.

The slag will contain gold and *a fortiori* silver if the conditions during fusion are favourable to oxidation of the metals. For this reason it is better to reduce almost all the litharge than to leave some of it in the slag, and the more readily oxidised metals—iron, manganese, &c.—must be reduced to their lowest oxides, ferrous oxide, &c. Practically all the copper, nickel, and other readily reducible metals will

then be in the lead button. In the case of ores containing much copper, this is a disadvantage, entailing loss of gold in cupellation, and the copper may be removed from the ore by treatment with acid before fusion (with some loss of silver) or large quantities of litharge (6 A.T. of PbO to 1 A.T. of ore) may be added, and only a small part of it reduced. In the latter case the slag contains gold and silver, and is cleaned by a second fusion, with the reduction of more lead. A similar method of fluxing is used for telluride ores, an excess of litharge in the slag preventing tellurium from entering the lead button. Antimonial and arsenical gold ores are sometimes roasted with coal-dust in a reducing atmosphere, in order to remove the antimony or arsenic as a sulphide before fusion. An alternative method is to fuse with much litharge and enough nitre to oxidise the antimony with the formation of antimoniates. Sulphides may be roasted in air before fusion.

The lead button, rounded by hammering, is placed on a hot cupel in the muffle (*see* p. 317), which is kept at a full red heat. The lead melts and oxidises, and the litharge and other oxides are absorbed by the cupel, the gold and silver being left as a bead (or ' prill ') on the surface. If the bead is large and contains much silver, it must be cooled gradually to prevent it from ' spitting ' on solidification, by which part of the metals might be lost. The bead is cleaned, weighed, flattened, and parted by dissolution in boiling nitric acid in a porcelain crucible or test-tube. If less than two parts of silver are present to one of gold, the metals are not parted completely, silver being left in the gold, and it is convenient to have a greater proportion of silver present. It is, therefore, often necessary to melt the bead with more silver, the proportion varying with the size of the bead, as follows :—

Weight of gold		Silver required for parting
10 milligrams		40 milligrams
1	,,	6 ,,
0·2	,, or less	2 ,,

A little extra silver is permissible, but if too much silver is present, there is a tendency for the gold to break up into very fine particles, which are difficult to wash without loss. The separation of these minute particles is avoided by dropping the bead into boiling acid, sp.gr. 1·2, when the parting will be completed in a few seconds. The parted gold is washed free from silver nitrate, &c., and is made firm and coherent for weighing by being annealed at a red heat. (For weights, balances, &c., *see* p. 318.) The silver is estimated by difference. The litharge, fluxes, &c., must be tested for silver and gold by running blank charges without ore.

In *scorification* about 0·1 or 0·2 A.T. of ore is mixed with 30 or 40 grams of granulated lead, and transferred to a dry scorifier (see Fig. 5). The charge is covered by a similar amount of granulated lead, and from 0·5 to 1 gram of borax is sprinkled on last. The scorifying dish is then charged into a muffle, which has been raised to a temperature of 1000°–1100°, or considerably above that required for cupellation, and the muffle is closed. As soon as the charge is melted down, the muffle is opened. The lead now oxidises, and the litharge, forming a ring of slag round the scorifier, oxidises the sulphides, &c., and slags off the earthy materials in the ore.

As oxidation proceeds, the litharge encroaches on the ' eye ' of metal, and at length covers it over. A pinch of charcoal powder is then added in tissue paper, and when the fusion is again tranquil, the charge is poured into a mould, and the slag detached. The lead is cupelled, and the assay finished as before.

In cupellation some gold and silver is carried into the cupel with the litharge, especially if tellurium, selenium, copper, &c., are present. The gold and silver are usually recovered by fusing the crushed cupel with litharge, charcoal, sodium carbonate, borax, and fluorspar, and cupelling the button of lead (see Lodge's Notes on Assaying, 112–169).

Assay of gold bullion and alloys. A piece of the metal to be examined is adjusted by cutting and filing to correspond in weight with a standard weight marked ' 1000,' which varies with different assayers between 5 and 10 grains, but is usually 0·5 gram. To the assay piece is added a piece of silver (free from gold) equal in weight to 2½ times (at the Royal Mint 2·1 times) that of the gold estimated to be present in the alloy, which, if not already known, can be ascertained by a rough preliminary assay or by the touchstone (*see* p. 324). The whole is wrapped in sheet lead, the weight of which depends mainly on the amount of copper to be removed, and varies from 8 to 32 times the weight of metal taken for assay. The lead packets are then transferred by means of tongs to cupels already raised to a bright red heat in the muffle, the current of air through the muffle is carefully regulated and the heat maintained. In from 10 to 20 minutes, a rapid passage of brilliant iridescent bands of colour over the surface of the button is observed to take place, and the buttons then appear to become colder, no longer glowing brightly with the oxidation of the lead. A few minutes later the muffle is closed to allow the buttons to set without loss by spitting. If copper is present in the assay pieces, however, this is not to be feared, and the charge can be drawn while the buttons are still molten. At the Royal Mint a charge consists of 72 assay pieces, which are charged in simultaneously by means of a divided metal tray with a sliding bottom and withdrawn simultaneously while still molten by means of a tray made of a mixture of graphite and clay, on which the cupels are placed. The buttons are cleaned by brushing, flattened on an anvil, annealed in the muffle or before a blowpipe, and reduced to a thickness of about 0·2 mm. by passage through a small pair of flatting rolls. The ' fillets ' are again annealed and coiled into a spiral or ' cornet' by the finger and thumb.

The parting in nitric acid is effected either in glass parting flasks or in a platinum boiling apparatus. If parting flasks are used, an amount of about 2 oz. of nitric acid of sp.gr. 1·2 is heated in the flask almost to boiling, and the cornet is then dropped in and boiled until 2 or 3 minutes after the red fumes have disappeared. The acid is then poured off, and the gold, after being washed twice with boiling water, is boiled for a further 15 minutes with nitric acid of sp.gr. 1·2 or stronger. The acid must be free from silver, chlorine, &c.

The gold is again washed, and is then transferred to a porous crucible or ' annealing cup '

by filling the flask with water, placing the cup over its mouth, and inverting it. The gold falls into the cup, and the flask is removed without agitating the water in the cup. The gold is then dried, annealed by heating to redness, and weighed. If no more than three parts of silver are present to one of gold, the cornet does not break up; and if enough is known previously of the composition of the bullion to make sure of this in the cupelled button, a platinum tray, containing a number of little platinum cups may be used. A cornet is placed in each cup, and the whole tray is immersed in nitric acid, and subsequently washed by dipping in and out of hot water. Less acid is used per assay piece by this method, and the boiling is more prolonged, 30 minutes in each of two acids of sp.gr. 1·23 being used at the Royal Mint.

In each batch of assays, two or more check assays on pure gold are made to determine the ' surcharge ' or net sum of the losses of gold and the gain in weight due to the retention of silver. With alloys boiled separately in flasks, check assays are of comparatively little value (see Rose's Metallurgy of Gold, 5th ed. 470–498).

Alloys of gold and silver If the alloy contains enough silver to be parted by nitric acid, no difficulty arises. The silver is dissolved, precipitated by hydrochloric acid, and weighed either as chloride or as metal. If the silver is deficient in quantity, the alloy is melted with two and a half times its weight of cadmium under a cover of potassium cyanide and parted with nitric acid. The silver is precipitated and weighed as chloride. The gold residue is annealed and weighed. Sometimes the silver i determined by difference, the alloys bein cupelled and weighed, and subsequently cupelle again with the addition of silver, and parted.

(For alloys containing *gold and platinum, see* p. 327.)

Assay by the touchstone. This ancient method consists in comparing the colour of the streak produced by a sample of gold of unknown composition on a black surface with those from a series of known compositions, after all have been treated alike with nitric acid. Any abrading surface on which the acid is without action can be employed for this purpose.

Iridium occurs alloyed with platinum, an finds its way into gold bullion. In the latter case, it is found with the gold cornet obtaine in the bullion assay, adhering in the form o black scales or powder to that side of the gol which was originally nearest to the cupel. I can be estimated by dissolving the gold in *aqu regia*, the iridium remaining undissolved.

Iron. The dry assay of iron, made by fusing ores with fluxes in carbon-lined (brasqued, crucibles, is obsolete, and need not be described. The wet methods are volumetric, based on the oxidation of iron from the ferrous to the ferri state or on the converse reduction. Either the bichromate or the permanganate method i generally used to determine the total amoun of iron in ores or the amount of iron present in the ferrous condition. The stannous chlorid method is used for measuring the amount iron present in the ferric state in an ore.

For the determination of the total amoun of iron, the ore is passed through an 80-mesl sieve, and attacked by acids as usual. Mos

res are oxides, carbonates, &c., and the iron in hem is easily dissolved by hydrochloric acid.

Titaniferous ores are fused with acid potassium sulphate and dissolved in water and ydrochloric acid. If nitric acid is present in he acid solution, it is destroyed by evaporating o dryness with hydrochloric acid and taking p with hydrochloric acid and water, and the ron is then reduced by zinc, which gives a stream of hydrogen or (if titanium is present) by rystals of sodium sulphite in a neutral or slightly icid solution. As soon as the solution is colourless, the excess of zinc is removed, or the sodium ulphite decomposed by boiling with hydrochloric acid, and titration is carried out in a orcelain basin by means of a solution prepared y weighing out 4·39 grams of potassium bichromate to the litre, equivalent to 5 grams of iron iccording to the equation :

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl$$
$$= 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O.$$
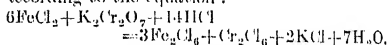
Potassium ferricyanide (0·1 p.c. solution, reshly prepared) is used as an indicator, a drop rom the assay solution being mixed with a drop f the test solution on a white glazed tile, from time to time. The end-point is reached when a colour is no longer produced. The solution of bichromate is standardised by means of piano wire, which contains about 0·4 p.c. of impurities.

The permanganate method is carried out in a sulphuric acid solution, the equation being :

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4$$
$$= 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$
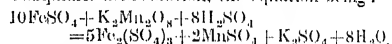
The standard solution is prepared by weighing out 2·82 grams of potassium permanganate per litre, which is equivalent to 5 grams of iron. The end reaction, the appearance of a pinkish tinge in the solution in the flask, is very sharp.

When the amount of ferrous iron only in the ore is required, the ore is dissolved in hydrochloric or sulphuric acid with exclusion of air. The ferric iron may be determined by difference, or, as a check, the stannous chloride method may be used, in which the yellow solution of ferric iron in hydrochloric acid is decolourised. The standard solution (20 grams of commercial stannous chloride per litre, acidulated with hydrochloric acid) is run into a boiling-hot solution of iron, and is standardised by means of a solution of ferric chloride free from nitric acid.

Analysis of iron and steel. The elements requiring estimation are carbon (graphite, combined carbon and total carbon), silicon, manganese, sulphur, phosphorus, arsenic, and, in special steels, chromium, nickel, tungsten, molybdenum, vanadium, &c. The total carbon is estimated by combustion, usually after removal of the iron by a cupric salt. The graphite is estimated by combustion of the residue after dissolving the iron in hydrochloric acid, by which the combined carbon is removed in combination with the hydrogen evolved, or more advantageously in nitric acid, by which the combined carbon is oxidised and retained in solution. The combined carbon is determined by the colour of a nitric acid solution compared with the colour of certain standard solutions containing known amounts of carbon. Silicon is weighed as silica after dissolution of the iron by acids or iodine. Sulphur is weighed as

barium sulphate, after the iron has been dissolved in *aqua regia*, or it is evolved as sulphuretted hydrogen, which is absorbed by caustic soda, and decomposed by a standard solution of iodine. The excess of iodine is estimated by sodium thiosulphate.

Manganese is separated by precipitation with bromine in an ammoniacal solution after removal of the iron as basic acetate. The precipitated hydrated peroxide is heated strongly in a muffle and weighed as Mn_3O_4. There is also a colorimetric estimation, the steel being dissolved in nitric acid and the solution boiled with lead peroxide. The colour of the permanganate produced is compared with those of standard solutions. Phosphorus is precipitated by ammonium molybdate or magnesia mixture. Arsenic is separated by precipitation as sulphide in an acid solution, converted into arsenic acid and determined by precipitation by magnesia mixture.

(For the determination of the metals in special steels, *see* under the headings *Chromium, Nickel*, &c. For full details of the analysis of iron and steel and also of the complete analysis of iron ores, *see* Blair's Chemical Analysis of Iron, Campredon's Guide Pratique du Chimiste Métallurgiste et de l'Essayeur, 438–634, and Brearley and Ibbotson's Analysis of Steel Works Materials.)

Lead. Both dry and wet methods of assay are used. The dry assay is only applicable to rich ores and to concentrates, and even with these is less accurate than the wet methods. The ore is crushed through a 60-mesh sieve, mixed with sodium carbonate and argol, and fused in a wrought-iron crucible or in a clay pot with hoop-iron. Galena is reduced by the iron, and any oxides, sulphates, &c., of lead are reduced by the argol. Borax is sometimes added as a cover. The following are examples of the charges recommended by Percy :

2. Any

	1. Rich galena, esp. galena	3. Phos-phate ore	4. Cerus-site
Ore	500 grs.	500 grs.	300 grs.	500 grs.
Sodium carbonate	500	350	350	500
Argol (tartar)	50	100	100	100
Borax	—	150	30	30

The iron crucible is made red hot, cleaned, and allowed to cool. The charge is then transferred to it, care being taken to avoid loss by dusting, and the borax, or, if none is used, part of the sodium carbonate is added as a cover. A clay lid is also placed on the crucible. The charge is slowly heated for about 20 minutes, and is then poured into a mould, provided that all signs of effervescence have disappeared, and the mixture is seen to be in a state of tranquil fusion. The lead is found at the bottom. It is detached from the slag with a hammer, and is cleaned and weighed. The slag is examined for lead beads before being thrown away. Clay crucibles are used for phosphate and carbonate ores.

When the ore contains arsenic, a speise is formed which is found adhering to the upper surface of the lead, below the slag. It must be removed with great care to avoid loss of lead. The lead should be soft and malleable. The silver and gold in the ore are determined by cupellation and parting (*see* p. 323). The

method gives results with pure ores which are about 1 or 2 p.c. too low. When the ore contains antimony, bismuth, copper, &c., these metals are in part reduced with the lead, and are weighed with it. If the lead button is hard, it is necessary to estimate the lead in it by weighing it as lead sulphate or otherwise, or to adopt wet methods of assaying the ore.

(For details of the dry assay of lead, see Percy's Metallurgy of Lead, 103–119.)

In the wet methods, oxidised ores are attacked by hydrochloric acid, followed by nitric acid, if necessary. Sulphide ores are treated direct with nitric acid. The lead is determined either as sulphate or volumetrically. by means of ammonium molybdate (Alexander's method). In the latter method (Eng. and Mng. J. April 1, 1893, 298), the mixture of nitric acid and ore is evaporated with sulphuric acid, diluted, boiled, and filtered. The lead sulphate in the residue is dissolved in hot ammonium acetate, acidified with acetic acid, raised to boiling, and titrated with a standard solution of ammonium molybdate, containing, according to Low, 4·25 grams per litre. The solution is standardised with pure lead foil. Tannin is used as an indicator, giving a yellow colour to a drop of the solution on a white glazed tile when the ammonium molybdate is in excess. If iron and calcium are present, it is better to separate the lead as sulphide and redissolve before titration (Low's Ore Analysis, 113).

Lead may also be determined in a feebly acid solution by adding an excess of potassium chromate and estimating the amount of excess by means of a standard solution of ferrous chloride. The reaction is the same as in the bichromate assay of iron, but in this case the end is marked by the appearance of a green colour in the test drops on the plate (Beringer's Assaying, 214).

Manganese occurs as MnO_2 in pyrolusite, when the value of the ore usually depends on its property of liberating chlorine when heated with hydrochloric acid, and not on the proportion of metal contained in it. Nevertheless, the percentage of manganese in ores is sometimes required, and spiegeleisen, ferromanganese, and steel are also assayed for manganese. Either the ferrous sulphate assay or Volhard's volumetric process is generally used. In the latter method, the manganese is precipitated by potassium permanganate in a boiling neutral solution. The precipitate, as far as numbers are concerned, is represented by the equation :

$$K_2Mn_2O_8 + 3MnSO_4 + 2H_2O$$
$$= K_2SO_4 + 5MnO_2 + 2H_2SO_4.$$

About one gram of the ore or spiegeleisen is dissolved in hydrochloric and nitric acids, heated with sulphuric acid, and neutralised by the addition of an emulsion of zinc oxide in slight excess. All the iron is precipitated, and, after violently shaking the mixture, it is made up to 500 c.c., allowed to settle, and 100 c.c. of the clear supernatant liquid is drawn off, heated to boiling, and titrated. The end point is marked by the appearance of a pinkish tinge. (For the estimation of manganese in steel, *see* above.)

Mercury. The wet methods of assay are not satisfactory, and one of the distillation methods is usually employed. When a large percentage

of mercury is present, a combustion tube of 18–20 inches long is used. It is sealed at one end and magnesite powder placed in it first, to a depth of 3 or 4 inches. Next a layer of 2 inches of unslaked lime is added and then 5 or 10 grams of ore well mixed in a mortar with 10 grams of lime. The mortar is cleaned with more lime and the rinsings added to the tube and covered with clean lime to a depth of 3 or 4 inches. Finally, a loosely fitting plug of asbestos is inserted and the unoccupied portion of the tube is drawn out almost to a point and bent over at right angles. care being taken that no hollow in the glass is formed which might collect some of the mercury. The tube is placed in position in a combustion furnace and tapped until the mixture settles and leaves a free passage for gases throughout its length. The narrow opening is made to dip into a beaker of water, and the tube is heated, beginning with the asbestos plug and finishing with the magnesite, which yields enough carbon dioxide to sweep out the vapours of mercury. The time required for heating is about 30 minutes. While the tube is still red hot throughout its length, its end is cut off and dropped into the beaker. The mercury collects in the water, and is dried by blotting-paper and then in a desiccator and weighed in a porcelain crucible.

When only small quantities of mercury are present, Eschka's method is used (Dingl. poly. J. cciv. 74), in which the mercury is condensed on a weighed piece of gold. This is in the form of a basin made of thin sheet gold, used as the cover of a porcelain crucible and filled with water to keep it cool. The basin projects beyond the rim of the crucible, and usually weighs about 10 grams. From 0·2 to 2·0 grams of ore is mixed with 1–4 grams of iron filings, and heated in the crucible for 10 or 20 minutes, the flame being kept from heating the upper part. This may be done by fitting the crucible into a hole in a piece of sheet asbestos. The gold basin is then dried without the agency of heat, and weighed, the increase of weight representing the mercury.

Molybdenum in ores is estimated by precipitation as mercurous molybdate in a very slightly alkaline or neutral solution by means of mercurous nitrate. The precipitate is ignited in a porcelain crucible, either alone or with litharge, until the mercury is expelled. The increase in the weight of the crucible is taken as MoO_3, but if chromium, vanadium, tungsten, phosphorus, or arsenic is present in the ore, the ignited MoO_3 must be purified by further treatment or separated before precipitation. Molybdenum in steel is precipitated as ammonium phospho-molybdate.

Nickel and **cobalt** occur together in ores, the former more commonly and in greater proportion than the latter. They are usually assayed together. In the fire assay, the ore is roasted sweet and then fused with arsenic to form a speise. This is heated in air on a little clay dish in the muffle, and the metals oxidised successively, iron passing into the slag first, cobalt next, and then nickel, copper being left until last. The changes in colour of the borax slag show the progress of the assay. The slag is coloured brown while iron is passing into it, blue by cobalt, sherry-brown by nickel, and blue by

copper. Gold is added to the speise after the elimination of cobalt if copper is present. The speise is weighed after each metal has been removed. The slag must be frequently examined and renewed, and great care and experience are needed to attain even approximate results.

The method is easier to carry out if copper is absent, and this metal is sometimes removed by precipitation with sulphuretted hydrogen in an acid solution before the speise is formed. If cobalt is absent, a weighed amount may be added, as otherwise it is difficult to observe the point at which nickel begins to pass into the slag after the removal of the iron. The arsenides in the speise have the formulæ Fe_2As, Co_2As, Ni_2As, and Cu_2As (Rhead & Sexton's Assaying, 187).

In the wet methods it is usual to roast the ore as a preliminary in order to remove the arsenic, sulphur, &c., and then to separate the nickel and cobalt from the iron, manganese, zinc, &c., by suitable methods. The nickel is precipitated as hydrate and weighed as NiO. Cobalt is often included in the nickel, but is separated if present in large quantities. A volumetric method depends on the interference by nickel in the titration of cyanide with a standard solution of silver nitrate. An alkaline solution containing caustic soda is used, and a little potassium iodide added as an indicator. An excess of a standard solution of potassium cyanide is added to a solution of nickel sulphate made alkaline (and precipitated) by caustic soda. The excess of cyanide is titrated by a standard solution of silver nitrate (Beringer's Assaying, 255). The reactions are represented by the equations :

$$4KCy + NiSO_4 = K_2NiCy_4 + K_2SO_4.$$
$$2KCy + AgNO_3 = KAgCy_2 + KNO_3.$$
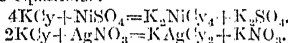
Nickel and cobalt are also sometimes estimated by electrolysis, and for this purpose must be separated from zinc and other metals, dissolved in nitric acid, and precipitated in an ammoniacal solution.

For the separation of nickel from cobalt, *see* J. Soc. Chem. Ind. ix. 375.

Nickel in steel is precipitated by bromine water and caustic soda, after removal of the iron as basic acetate. It is weighed as NiO.

Platinum in alluvial deposits is concentrated by panning, as in the case of auriferous sands. In all cases platinum can be collected in lead by the same methods as those described under the assay of gold ores. The lead buttons are sometimes cupelled at a very high temperature, but it is difficult to remove the whole of the lead in this way, as the 'prill' freezes on the cupel when only part of the lead has been oxidised.

Cupellation may be finished in the oxygen-gas blowpipe flame, but the loss of platinum is then large. It is more usual to dissolve the lead button in dilute nitric acid and to filter off the platinum and gold residue, which is parted by dissolving in *aqua regia*, and precipitating the gold with oxalic acid. The platinum is estimated by difference or by precipitation as $(NH_4)_2PtCl_6$.

Platinum in alloys or in rich alluvial concentrates may be estimated by melting with six parts of pure lead, and grinding in a mortar the brittle alloy freed from slag. Portions of the alloy are scorified with fresh lead and dissolved in nitric acid.

Alloys containing gold, silver, and platinum are difficult to assay, as they are insoluble in *aqua regia.* The method adopted is first to cupel the alloy to remove copper, &c., these metals being estimated by difference. The alloy is then inquarted by cupellation with twice its weight of silver and parted by boiling in sulphuric acid. The residue contains the gold and platinum. These may be parted by again inquarting with silver and dissolving in nitric acid, provided that the amount of gold present is at least ten times that of the platinum. If the proportion of gold present is less than this, part of the platinum remains undissolved, and it is therefore necessary to add gold in many cases. The parted gold is weighed and the platinum estimated by difference (6ème Rapport des Monnaies, 1901, p. xxix.; Rose's Precious Metals, 272).

Silver. The ores of silver are assayed in the same way as those of gold of a similar kind, the scorification method being used far more frequently than in the case of gold ores. The slags and cupels must be examined usually, as silver is more readily lost than gold. The temperature of cupellation is kept as low as possible, to check the loss of silver by volatilisation (see Lodge's Notes on Assaying, 37–111).

Silver bullion and alloys are assayed by cupellation, by the Gay Lussac or the Volhard volumetric processes, or by weighing the chloride (India Mint method). In cupellation, the ' base ' or oxidisable metals are removed in the muffle, and the silver prill is cleaned and weighed. The weight of silver taken is usually 10 grains. The amount of lead required varies from six times the weight of the silver for alloys of high standard to twelve times for silver 700 fine. The method is not suitable for alloys containing less than 70 p.c. of silver. The muffle is kept at a lower temperature than that required for gold cupellation, but must be raised to above the melting-point of pure silver (962°) at the finish, to prevent the metal from setting in the furnace before all the lead has been removed. When the cupellation is complete, the mouth of the furnace is closed with great care to exclude draughts, and the furnace is allowed to cool slowly to prevent loss of silver by spitting. The solidified prills are cleaned and weighed. The loss of silver in cupellation varies from 5 to 15 parts per 1000, and check assays on pure silver are placed in all parts of the furnace to measure this loss. Any gold that may be present is weighed as silver. The process is very ancient, and clear reference is made to it in connection with a trial of the Pyx in the Black Book of the Exchequer, written in the reign of Henry II.

In the Gay Lussac process, the volume is measured of a standard solution of common salt or sodium bromide required for the precipitation of a little more than a gram of silver in solution as nitrate. No indicator is used, and the end of the operation is judged from the appearance of a faint cloud of chloride in a solution from which almost all the silver has been precipitated. It is the most accurate method of assaying silver bullion. The standard solution of common salt (usually called the ' normal solution ') contains about 5·416 grams of NaCl per litre, so that 100 c.c. will precipitate 1 gram of silver. A weight of silver bullion con-

taining about 1·003 gram of silver is weighed and dissolved in nitric acid, and 100 c.c. of the salt solution added to it from a pipette. The chloride is agglomerated by a shaking in a stoppered bottle, and the clear supernatant liquid is tested by ' decinormal ' solutions of common salt and, if necessary, of silver nitrate. The appearance of the cloud of silver chloride shows the amount of silver left in solution. Further shakings are resorted to if required, and the final reading is taken after waiting for about 5 or 10 minutes. Check assays on fine silver are used with every batch to test the strength of the solution, which varies with the temperature, &c. Mercury interferes with the method, and is detected by the colour of the precipitated silver chloride, which does not darken if mercury is present. Acetate of soda corrects the error if the quantity of mercury present is small. The Gay Lussac method can be used only in cases where the approximate assay is already known (Percy's Silver and Gold, 282; Riche et Forest, L'Art de l'Essayeur, 183).

In the India Mint method, the silver alloy is dissolved in nitric acid and precipitated by a slight excess of hydrochloric acid. The silver chloride is then collected by shaking in a stoppered bottle, and, after being washed, is transferred to a porous cup, dried, and weighed while warm. The chloride is washed by decantation, but the drying is tedious, and is expedited by breaking up the crust with a glass rod. Any gold that may be present is weighed as silver chloride. This is the best method for alloys containing less than 70 p.c. of silver (Trans. Inst. Mng. & Met. xvii. 334).

The Volhard method is largely used in this country. The nitric acid solution of the silver is freed from nitrous acid by boiling, and is then diluted and titrated with a solution containing 7·04 grams of ammonium thiocyanate per litre. As this salt is deliquescent, it is usual to weigh out about 7·3 grams per litre. Iron alum is used as an indicator, giving a red colour when all the silver has been precipitated. Time is saved and the accuracy of the method increased by taking for assay an amount of alloy containing about 1·003 gram of silver, and running in 100 c.c. of the standard solution of thiocyanate from a pipette. After shaking the liquid in a flask, the titration is finished by adding the thiocyanate a drop or two at a time. Check assays on fine silver are used (Trans. Inst. Mng. & Met. xvi. 154).

Tin. Tin ore is concentrated on a vanning shovel with the production of ' black tin ' in order to determine what yield may be expected when the ore is treated on the dressing floors. The ore is crushed and sampled, and about 30 grams are thoroughly mixed with 30 or 40 c.c. of water on the vanning shovel with the fingers, to prevent, as far as possible, the loss of ' float tin.' The ore is then collected by a vigorous circular motion of the water, and the slimes are poured off, a process which is repeated until the water remains clear after being left to settle for a few seconds. By means of a circular motion of the shovel, combined with a series of jerks, the tin oxide is now separated from the lighter material, which is carried down by the descending wave. The tailings are saved and washed over again until they yield no more tin,

and are then crushed by rubbing with a hammer and again washed. The concentrates are dried and roasted and dressed once more. Sometimes they are washed quite clean from worthless material, and sometimes left impure with oxide of iron, &c., according to the nature of the ore and the custom of the operator. Sometimes they are purified by boiling in hydrochloric acid or *aqua regia*, which, according to J. H. Collins, causes a loss of tin. The residue is usually reported in pounds of black tin to the long ton of ore, or alternatively in parts per 200, so that a produce of ' 9½ ' would be equivalent to 4·75 p.c. (Beringer's Assaying, 276).

The black tin obtained by vanning is assayed for metallic tin by reduction with anthracite (Cornish method) or potassium cyanide. In the Cornish method 100 grams of tinstone are heated with 20 grams of anthracite in a plumbago crucible at a white heat for 15 or 20 minutes. The charge is then stirred with a stick and again heated for a few minutes before pouring. The excess of anthracite contains beads of tin, which are separated by vanning. In the cyanide process, 10 grams of tinstone are fused with 40 grams of impure cyanide (containing potassium carbonate), and poured at a red heat. The German process consists in reducing a mixture of 5 grams each of tinstone and cupric oxide with 15 grams of black flux (a mixture of carbon and potassium carbonate, obtained by heating tartar) and 1·25 grams of borax with a cover of common salt. The reduced metal is compared in weight with that of the copper reduced from cupric oxide alone. The most trustworthy of these methods is the fusion with cyanide. The reduced tin, however obtained, is usually impure (Beringer's Assaying and Kerl's Metallurgische Probirkunst).

A good wet method for the estimation of tin in ores without previous concentration is described by G. L. Mackenzie (Trans. Inst. Mng. and Met. xiii. 1904, 87). It consists in cleaning a sample of from 1 to 5 grams of the ore with *aqua regia* (and removing the tungstic acid, if it is present, by means of ammonia), reducing the stannic oxide to tin by ignition in a current of coal gas, dissolving the metallic tin with hydrochloric acid and potassium permanganate, precipitating with sulphuretted hydrogen, and igniting the tin sulphide. The tin is weighed as stannic oxide.

Tin is also estimated volumetrically. A satisfactory method described by Beringer (Text-Book of Assaying, 11th ed. 285) is to reduce the solution of stannic chloride to stannous chloride by means of nickel foil, and to titrate with a standard solution of iodine in an atmosphere of carbonic acid gas. Starch is used as an indicator. In all wet methods, tin oxide must be reduced to metallic tin before it can be dissolved.

Titanium in ores is generally in the form of titanic oxide, which is insoluble in acids. Titanates, however, are somewhat soluble, so that on attacking ores with acid, titanium will be found partly in the residue and partly in the solution. The metals of the iron group with titanium are precipitated from the solution as basic acetates, which are fused with potassium bisulphate and extracted with water. The titanic acid is precipitated from the solution

by means of prolonged boiling with sulphurous acid. The residue left by the attack on the original ore with acids is similarly treated, after the silica has been removed by heating with sulphuric and hydrofluoric acids (Beringer's Assaying, 293).

Tungsten in wolfram, steel, &c., is estimated by weighing as tungstic acid WO_3. The ore is boiled with hydrochloric acid or *aqua regia*, when the tungsten separates as insoluble yellow tungstic acid. After thorough washing, this is dissolved in ammonia, filtered, and recovered by evaporating the solution to dryness, and gently igniting the residue to decompose the ammonium tungstate. Nearly pure tungstic acid remains. Any silica that may be present may be removed by hydrofluoric acid.

Uranium. The mineral is evaporated with nitric acid and taken up with HCl. After separation of the other metals as sulphides and carbonates, the uranium is precipitated by ammonia and weighed as U_3O_8, or it is precipitated by microcosmic salt in the presence of acetic acid and ammonium acetate. The precipitate consists of ammonium uranyl phosphate $UO_2NH_4PO_4$ which is washed, ignited gently and weighed or converted into uranyl pyrophosphate $(UO_2)_2P_2O_7$, for greater accuracy (Low's Technical Ore Analysis, 201). This precipitation is also the basis of a volumetric method, a boiling solution of uranium being titrated with a standard solution of phosphate, until ferrocyanide no longer gives a brown colour.

Vanadium in steel is estimated by titrating with potassium permanganate. The steel is dissolved in HCl and evaporated to dryness with a little nitric acid. The residue is fused with nitre and fusion mixture, boiled in water and filtered, and the filtrate evaporated with H_2SO_4, reduced by sulphur dioxide and titrated. One atom of iron is equivalent to one of vanadium in the titration (Rhead and Sexton's Assaying, 270).

Zinc. The old dry methods of assay of ores and alloys based on the loss of weight due to the volatilisation of zinc at a white heat are obsolete. Zinc is usually weighed as oxide after precipitation as carbonate, or it is titrated with sodium sulphide or potassium ferrocyanide. An amount of 1 or 2 grams of ore is weighed out and dissolved in hydrochloric acid or *aqua regia*. The silica and metals other than zinc are removed as usual. All the precipitates will contain zinc if they are bulky, and must be redissolved and reprecipitated. The alkaline filtrate may be diluted to 200 c.c. and used for the sodium sulphide titration, which is carried out at 50°–60°. A flake or two of freshly precipitated ferric hydrate is used as an indicator, turning from red to black as soon as sodium sulphide is in excess. One c.c. of the standard solution of sodium sulphide should be equal to 0·01 gram zinc. Instead of ferric hydrate, sodium nitroprusside may be used as an indicator on a white tile. This gives a purple colour with sodium sulphide.

For titration with potassium ferrocyanide, the pure ammoniacal solution of zinc obtained as above is acidified with hydrochloric acid, boiled and titrated hot. The standard solution of ferrocyanide is made up by dissolving 41·25

grams of the pure salt in a litre of water. The test solution consists of 0·5 gram of uranium acetate dissolved in 20 c.c. of water. A drop of this solution gives a brown colour on a white tile with a drop of the zinc solution as soon as the ferrocyanide is in excess. It is advisable to confirm the end reaction by adding 5 c.c. of a standard solution of zinc in hydrochloric acid, containing 10 grams of zinc per litre, and again titrating (Chem. News, lxxvi. 6).

The assay of zinc-dust for metallic zinc is made by acting on the sample with dilute sulphuric acid, and collecting and measuring the hydrogen which is evolved.

Commercial metallic zinc contains lead, cadmium, and iron, and may also contain arsenic, copper, antimony, tin, &c. By dissolving in dilute sulphuric acid, the lead and the greater part of the copper, tin, cadmium, &c., are left undissolved. The residue is attacked by nitric acid, and the metals separated as usual. Iron in zinc is titrated in the sulphuric acid solution without being separated. Arsenic and antimony are passed with the hydrogen evolved by sulphuric acid into a solution of silver nitrate (Campredon, Guide Pratique, 760; Eliot and Storer, Amer. Acad. Arts & Sciences, viii. 57).

Coal. The assay of coal usually comprises the determination of moisture, total ash, sulphur, coking properties, and calorific power. The coal is broken down and sampled as in the case of ores (see p. 316), and the sample is passed through an 80-mesh sieve.

The moisture is determined by drying 1 gram in a water-oven for 30 minutes and weighing. The coal is then again warmed for 15 minutes and reweighed, and the process is continued until the weight is constant or begins to increase.

For sulphur, 2 grams of coal are mixed with 3 grams of a mixture of two parts of calcined magnesia and one part of potassium carbonate, and heated to dull redness for an hour in a porcelain or platinum crucible, with occasional stirring. After cooling, the charge is transferred to a beaker and digested with water and 1 c.c. of bromine. It is then acidulated with hydrochloric acid, the bromine boiled off, and the sulphur, now in the form of sulphate, precipitated by barium chloride. The sulphur may also be oxidised by heating the coal with a mixture of nitre and common salt. Phosphorus in coal, if determined at all, is estimated in the ash, which may require complete analysis.

The coking qualities of coal are examined by heating 50 grams of coarsely crushed coal in a 'large copper' crucible covered with a closely fitting lid. The evolution of gases is completed after 15 or 20 minutes at a full red heat. After cooling, the coke is turned out and weighed, the loss of weight giving the amount of volatile matter.

The calorific power of coal is determined by igniting 2 grams of the finely powdered sample with 20 grams of a mixture of six parts of potassium chlorate and one part of nitre. The coal and deflagrating mixture are ground together in a mortar and ignited in a Thompson calorimeter. The error due to loss of heat by escaping gases, &c., is always taken as one-tenth of the total evolved. The calorific power reported is

the weight of water that could be evaporated at 100° and 760 mm. pressure by a unit weight of the fuel (v. FUEL).

Cyanide solutions. In gold mills, these solutions are in wide use, and require frequent analysis. Free cyanide is estimated by means of a solution of silver nitrate prepared by dissolving 13·04 grams of crystallised $AgNO_3$ in a litre of water. One c.c. of this solution is equivalent to 0·01 gram of KCy, the end of the titration being denoted by the solution becoming milky from the precipitation of AgCy. The reaction is represented by the equation :

$$AgNO_3+2KCy=KAgCy_2+KNO_3.$$
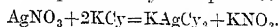
The amount of cyanide solution taken for assay may be from 10 c.c. to 100 c.c., according to its strength. Alkalis and other compounds which may be present dissolve silver cyanide, and accordingly it is usual to add potassium iodide as an indicator. Turbid cyanide solution must be filtered before titration. If soluble sulphides are present, they prevent the assay from being carried out. They are removed by agitating the solution with freshly precipitated lead carbonate. If zinc is present in the solution, part of the cyanide contained in the double cyanide K_2ZnCy_4 is estimated as free KCy.

The 'total alkali' in a cyanide solution is estimated (J. E. Clennell, Chemistry of Cyanide Solutions, 62) by titration with a standard solution of sulphuric acid, using methyl orange as an indicator. 'Protective alkali' (op. cit. 63) is determined by adding a slight excess of silver nitrate together with a little phenolphthaleïn solution, and titrating with sulphuric acid until the pink colour disappears. The 'reducing power' of cyanide solutions is determined by acidification and subsequent titration with potassium permanganate, until the pink tint becomes permanent, or by adding an excess of permanganate followed by an excess of potassium iodide and estimating the amount of iodine liberated (op. cit. 71).

Gold and silver in cyanide solutions are determined by evaporation on lead foil, which is afterwards cupelled, or by evaporation with litharge, which is fused for lead. A more rapid method is to precipitate the gold and silver with zinc-dust and sulphuric acid, filter, and scorify or fuse the residue. The latter method is especially suitable for treating large samples of poor solutions containing very little gold and silver. In all these methods, a button of lead is obtained which is cupelled and the gold and silver parted as usual.

Silica. The silica in ores is partly free and partly combined. The white sandy residue left after careful extraction with acids is sometimes nearly pure silica, and is often reported as 'silica and silicates insoluble in acids.' It may be tested with sulphuric and hydrofluoric acids. The usual method with ores, slags, &c., is to fuse 1 gram with 5 grams of fusion mixture and a little nitre in a platinum crucible or dish. It is extracted with warm water and a little hydrochloric acid and evaporated to dryness on a water-bath. The bases are dissolved out with hydrochloric acid, and the silica filtered off. The filtrate is again taken to dryness and dissolved in hydrochloric acid to separate the remainder of the silica. If the ore contains a

large percentage of sulphides, oxides, &c., which are soluble in acids, these are removed before the fusion. In this case the acid solution may contain silica, which is removed by evaporating to dryness, taking up with hydrochloric acid and filtering. The purity of the silica is tested by evaporating two or three times with water, sulphuric acid and hydrofluoric acid. The silica is volatilised (J. Amer. Chem. Soc. xxiv. 1902, 362).

Sulphur. A rapid method of determining the sulphur in ores given by Furman (Manual of Practical Assaying, 5th ed. 91) is to fuse 5 grams of the ore with 15 grams of borax, 3 grams of charcoal, and one or two nails in a hot fire. The time required for fusion is about 15 minutes. The nails are then withdrawn and the charge poured. As soon as the slag is cool, the matte is detached from it with a hammer and weighed. If the matte were pure FeS, it would contain 36·3 p.c. of sulphur. By analysis, Furman finds that the nearest approximation is to take the sulphur as 30 p.c. of the matte. The method, though inaccurate, is sometimes useful, as it can be completed in less than half an hour.

The more accurate methods consist in oxidising the sulphur by *aqua regia* or nitric acid and potassium chlorate, or by fusion with a mixture of nitre and sodium carbonate, and weighing it as barium sulphate. A good method for ores and slags consists in fusion with caustic alkali, extracting with water, and oxidising with bromine. After separation of the silica, the sulphur is precipitated by barium chloride (Chem. News, 1. 1884, 194). If lead is present, the solution is boiled with ammonium carbonate.   T. K. R.

ASTATKI. A Russian term, signifying 'dregs,' applied to the residue left in the distillation of Baku petroleum after the volatilisation of the kerosene, and now largely used as fuel in the Caspian region (v. PETROLEUM).

ASTERIA (*Star Sapphire*) v. CORUNDUM.

ASTRALINE. Russian petroleum oil, used for burning (v. PETROLEUM).

ASTRALITE. A glass resembling aventurine, but containing crystals of a cupreous compound which by reflected light exhibit a dichroic iridescence of dark red and greenish blue. Made by fusing and allowing to cool slowly a mixture of 80 pts. silica, 120 lead oxide, 72 sodium carbonate, 18 borax, with either 24 pts. scale oxide of copper, and 1 pt. scale oxide of iron, or with 5 pts. lime, 26 copper oxide, and 2 iron oxide.

ASTROLIN. Trade name for antipyrine-methyl-ethyl glycollate $C_5H_{10}O_3,C_{11}H_{12}ON_2$, m.p. 64°–65·5°. A colourless powder, with a slight smell and pleasant taste, readily soluble in water and alcohol.

ASUROL. Sodium-mercuri-amido-oxy*iso*-butyrosalicylate.

ASYPHIL. Trade name for a *mercury salt of p-aminophenylarsinic acid*

$$(NH_2C_6H_4AsO(OH)O)_2Hg.$$
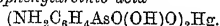
(v. ARSENIC, ORGANIC COMPOUNDS OF; *cf.* p. 337).

ATACAMITE. Hydrated oxychloride of copper $CuCl_2\cdot3Cu(OH)_2$, occurring in the Atacama region of Chile, sometimes in sufficient amounts for use as a copper ore (Cu 59·4 p.c.). Large quantities have also been mined at Wallaroo in South Australia. Orthorhombic

crystals of a bright-green colour and with brilliant faces are not uncommon. Sp.gr. 3·76. Before the days of blotting-paper, it was used, under the name of arsenillo, as a writing sand for absorbing ink (v. COPPER).   L. J. S.

ATELESTITE. A bismuth arsenate containing iron phosphate found at Schneeberg in Saxony : Bi_2O_3, 57·15 ; $Fe_2P_2O_6$, 12·50 ; As_2O_3, 30·35 (Freuzel, J. M. 1873, 785).

ATHAR or **ATTAR.** Indian name for volatile oil of roses (v. OILS, ESSENTIAL).

ATLAS DYNAMITE *v.* EXPLOSIVES.

ATLAS POWDER *v.* EXPLOSIVES.

ATLAS SCARLET *v.* AZO- COLOURING MATTERS.

ATMOSPHERE. The gaseous envelope surrounding any liquid or solid body ; more particularly the gaseous envelope which surrounds the earth, and which is commonly known as air. The thickness of this aërial envelope is not known even approximately, but it is quite certain that it exceeds 45 miles measured from the earth's surface, which was the limit assigned to it by Wollaston. Secchi calculated that air exists even at a height of 300 kilometres above the earth's surface. From the ratio of decrease of density with elevation, the atmosphere at a height of 50 miles cannot exert any measurable pressure. The mass of the atmosphere forms, like the earth itself, an oblate spheroid, the polar axis of which is much shorter than the equatorial axis, the ratio of the two axes being, according to Laplace, as 2 to 3.

The pressure of the atmosphere at any particular spot may be measured in terms of the height of a column of mercury which it is capable of sustaining. It follows from the law of Boyle that the density of the air rapidly diminishes with the height. For air of constant temperature, its density, or, what comes to the same thing, the height of the mercurial column, should diminish in geometric progression, whilst the distance from the earth increases in arithmetic progression. The pressure, even at the same place, is continually varying from a variety of causes, and hence the height of the barometer, as the mercurial column was first termed by Boyle, is practically never absolutely constant. The average height at any one spot at the sea-level is mainly dependent upon the great movements of air which result from the effect of the earth's motion upon the gaseous envelope, combined with variations in the density of the aërial mass due to solar action.

According to Regnault, 1 litre of dry air, free from carbonic acid and ammonia, measured at 0° and 0·76 mm. pressure, at Paris (lat. 48° 50′) and at a height of 60 metres above the sea-level, weighs 1·293187 grams. Lasch found that 1 litre of pure air at standard temperature and pressure weighs at Berlin (lat. 52° 36′) 1·293635 grams.

The Bureau Internat. des Poids et Mesures adopts for the weight of 1 litre of dry air, containing 0·04 p.c. carbonic acid, at the normal temperature, and under the normal barometric pressure at lat. 45° and sea-level,

$$P_{t,i} = \frac{1\cdot293052}{1+0\cdot00367} \times \frac{1}{760},$$

on the assumption that 0·00367 is the expansion coefficient of air at constant pressure for a normal degree. For purposes of ordinary chemical calculation it may be assumed with

sufficient accuracy that 1 gram of air measures at standard temperature and pressure 773 c.c.

The total weight of the atmosphere is about 11 trillions of pounds, or about 5 trillion kilograms and the relative amounts of the chief constituents may be assumed to be—

	Trillions kgm.
Nitrogen (argon, &c.)	4·041200
Oxygen	1·218040
Carbonic acid	0·003156
	5·262396

Herschel calculated that, allowing for the space occupied by the land above the sea, the mass of the atmosphere is about $\frac{1}{1260000}$ part of that of the earth.

The unit of pressure adopted by engineers and others, and styled an *atmosphere*, is an amount equal to the average pressure of the atmosphere at the sea's level. In British measure an atmosphere is the pressure equivalent to 29·905 inches of mercury at 32°F. at London, and is about 14·73 lbs. on the sq. inch. In the metric system it is the pressure of 760 mm. (29·922 inches) at 0°C. at Paris, and is equal to 1·033 kilos. on a sq. centimetre. Hence the English 'atmosphere' is 0·99968 that of the metric system.

The specific heat of air at constant pressure is 0·2374 (Regnault). Its coefficient of thermal expansion between −30° and 200° is 0·003665 for 1°.

By the application of sufficient cold and pressure, air may be liquefied.

Comparatively little of the sun's heat is absorbed in its direct passage through the air. According to Tyndall, a column of air 1 metre long absorbs 0·088 p.c. of the heat which passes through it. According to Violle, and also Lecher and Pernter, the amount is not greater than 0·0070 p.c. This absorption is mainly due to aqueous vapour, and, in a lower degree, to carbonic acid and suspended organic matter. The air mainly gets its heat by conduction from the earth, and hence, as a rule, it is hottest near the ground. The law of the decrement in temperature corresponding to height is not accurately known ; it is usually stated to be about 0·56° per 100 metres, but the rate is liable to very great variations.

Air is not perfectly transparent. Its particles reflect and scatter light in sufficient quantity to obscure the light from the stars. The blue colour of the sky is due to the fact that the most refrangible rays are most widely scattered. In the higher regions of the atmosphere, where the amount of reflected light becomes less and less, owing to the decreased density of the air, the sky appears to grow gradually darker. Brewster first proved that the blue light from the sky, as well as the white light from the clouds, was due to reflected light, by the fact that it was polarised.

Suspended matter, dust, smoke, aqueous vapour in a state of partial precipitation, &c., greatly diminish the transparency of air. Wild gives the following numbers as representing the transparency coefficient of 1 metre of air :—

Dry air (free from dust)	0·99718
Air of a room (dry, but containing dust)	0·99520
Air free from dust, but saturated with aqueous vapour	0·99328

The refractive indices of dry air at standard temperature and pressure for the Fraunhofer lines A, B, C, D, E, F, G, H, are, according to Kettler (Pogg. Ann. 124–401), as follows :—

nA=1·00029286	nE=1·00029584
nB=1·00029345	nF=1·00029685
nC=1·00029383	nG=1·00029873
nD=1·00029470	nH=1·00030026

The emission spectrum of air has been mapped by Huggins (Phil. Trans. 154, 139) and Angström (Pogg. Ann. 94, 141), and the spectrum of lightning by Kundt (Pogg. Ann. 135, 315), who has shown that forked lightning gives a line spectrum, whereas sheet lightning gives a band spectrum. The absorption spectrum of air was first mapped by Brewster and Gladstone, and has been further examined by Janssen, Cornu, and Chappuis (Compt. rend. 91, 988).

Air, owing to the oxygen it contains, is a magnetic substance. The diurnal variation in magnetic declination has been alleged to be due to the varying magnetic potential of the oxygen owing to alterations in temperature.

Air is a mixture of nitrogen, oxygen, aqueous vapour, argon, carbon dioxide, with minute quantities of ozone, hydrogen peroxide, ammonia, nitrous and nitric acids, hydrocarbons, helium, neon, krypton, xenon, hydrogen, &c. That the air is not a chemical compound of its component gases is proved by the facts : (1) that these gases are not present in any constant ratio ; (2) that air can be made by simply mixing its constituents in the proportion indicated by the analysis of air, without contraction or any thermal disturbance resulting ; (3) that on treating air with water and expelling the dissolved air by boiling, the proportion of the oxygen to the nitrogen is found to be increased, and in amount corresponding with the law of partial pressures : (4) that the constituents of the air can be mechanically separated by processes of diffusion ; and (5) that the refractive power of the air is equal to the mean of the refractive powers of its constituents, whereas in compound gases the refractive power is either greater or less than the refractive power of the elements in a state of mixture.

The amount of oxygen in air may be ascertained by measuring the diminution in volume which a known bulk experiences when in contact with some substance capable of absorbing or combining with oxygen gas. Among the substances which may be conveniently used for this purpose are :

1. *Phosphorus.* A fragment of phosphorus on the end of a platinum or copper wire is exposed to a measured volume of air standing over water or mercury until no further decrease of volume is observed (Berthollet). Lindemann (Zeitsch. anal. Chem. 1879, 18, 158) employs thin sticks of phosphorus for the same purpose in the Orsat apparatus (*v.* GAS ANALYSIS). At a temperature below 7° the oxidation of the phosphorus ceases.

2. *Pyrogallol in Alkaline solution.* Chevreul, in 1820, first suggested the use of this reagent. The absorption is apt to be accompanied by the formation of notable quantities of carbon monoxide if the amount of oxygen is large or the alkaline solution very concentrated. According to Hempel (Ber. 20, 1865), the best proportions are 5 grams pyrogallol dissolved in 15 c.c.

water mixed with 120 grams caustic potash dissolved in 80 cm. of water. Practically, no carbon monoxide is formed with this solution. The absorption is very rapid (Hempel, Ber. 18, 267 and 1800).

3. *Metallic Copper.* A spiral of copper wire is heated to redness in dry air free from carbonic acid and of known pressure until the whole of the oxygen has combined with the metal to form cupric oxide. The pressure of the residual gas is then determined, whereby the amount of nitrogen is ascertained, and hence the amount of oxygen. An apparatus on this principle was suggested by Jolly (W. N. S. 6538) ; it is seen in Fig. 1.

The glass vessel A, of about 100 c.c. capacity, is exhausted by the mercurial pump, and is replenished with the air under investigation. This is then cooled to 0° by surrounding A
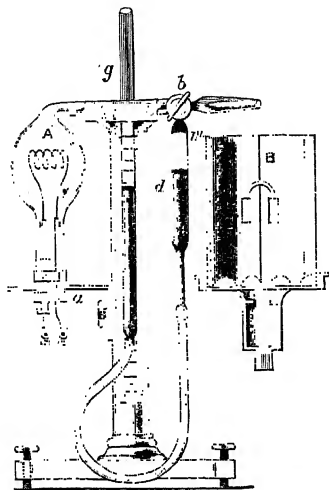
Fig. 1.

with the metallic cylinder B, which is filled with melting ice. The tension of the confined air is measured by the height of mercury in the glass tubes g and d, which are connected together by caoutchouc tubing. The tube g is movable in the clamp f, the position of d being fixed with reference to A. By turning the three-way stop-cock b, A and d may be alone brought into connection, or both may be made to connect with the outer atmosphere. The cock is now so turned that A and d are alone in connection ; the tube g is now raised until the level of the mercury in d just touches the point m, when the tension of the air is read off on the graduated scale behind g. The copper spiral in A is next heated to redness by an electric current, whereby the heated metal rapidly combines with the oxygen. The cylinder B is once more placed round A, the residual nitrogen cooled down to 0° by means of melting ice, and its tension measured by adjusting the level of the mercury to m, and reading off the height of the mercury in g. If, for example, the pressure before abstracting

the oxygen was 702·56 mm., and after the abstraction was 555·70 mm., then 1 volume of the air would be reduced to $=\frac{555\cdot70}{702\cdot56}=0\cdot79096$ vol., or, expressed centesimally, the composition of the air would be :

Nitrogen (argon, &c.)	.	.	79·096
Oxygen	.	.	.	20·904

100·000

Kreusler has shown that unless the air be carefully dried before being heated with the copper spiral, the proportion of oxygen will be apparently too low.

Dumas and Boussingault (Ann. Chim. Phys. [3] 3257), as far back as 1841, made use of the fact that heated metallic copper combines with oxygen, in order to determine the gravimetric composition of air. Air deprived of moisture and carbonic acid was passed through a weighed tube containing metallic copper heated to redness, whereby all the oxygen was absorbed, the nitrogen being collected in a vacuous glass globe also previously weighed. At the conclusion of the experiment the tube containing the metallic copper was again weighed ; the increase in its weight gave the amount of absorbed oxygen, together with the weight of the nitrogen which it also contained. The nitrogen was then removed by the air pump and the tube again weighed ; the difference between the first and third weighings of the tube containing the copper gave the weight of absorbed oxygen, and the weight of nitrogen was obtained by adding the difference between the second and third weighings of the tube to the increase in the weight of the glass globe. As the mean of a large number of experiments made by this method, the precentage composition by weight of air free from water and carbonic acid was found to be

Oxygen .	.	.	.	23·00
Nitrogen (with argon, &c.)	.	77·00

100·00

Leduc has shown that this proportion of oxygen is too low, as an average ; the amount is about 23·2 p.c. by weight as calculated from the known density of air and of its constituent gases (Compt. rend. 1896, 12, 1805 ; 1898, 126, 413).

4. *Explosion with hydrogen.* A measured volume of air is mixed with a known volume of hydrogen in excess, and the mixture is exploded by the electric spark, when the oxygen combines with the hydrogen in the proportion of 1 vol. of the former to 2 of the latter to form water. One-third of the contraction resulting from the explosion represents, therefore, the amount of oxygen in the air under examination. This method, first suggested by Volta, was perfected by Bunsen. Modifications of the method have been made by Regnault and Reiset, Williamson and Russell, Frankland and Ward, and others. These methods are extremely accurate, and have afforded us all the exact knowledge we have respecting the variations in the amount of oxygen in atmospheric air. Thus Bunsen, in a series of analyses made in the winter of 1846, found that the percentage amount varied from 20·97 to 20·84. Regnault made a large number of analyses of air collected from all parts of the

world. In 400 analyses of air collected in Paris the minimum amount of oxygen was 20·913, the maximum 20·999. Air collected in various parts of Europe, from above the Atlantic Ocean, from the summits of the Andes and from the South Polar Sea, contained an amount of oxygen varying from 20·86 to 21 p.c. Many hundreds of analyses were made by Angus Smith, of air collected in various towns in England and Scotland, and also of air collected in the country. The oxygen in London air varied from 20·857 to 20·95, less oxygen as a rule being found in the air of streets than in that of the parks and open spaces. A series of 30 analyses of Glasgow air showed variations from 20·887 in the closer parts to 20·929 in the more open spaces. Even wider extremes were found by Leeds in the air of New York, viz. from 20·821 to 21·029 p.c. According to E. W. Morley, the diminished proportion of oxygen may be caused by the down-rush of air from the higher regions of the atmosphere, which probably contain a less relative amount of oxygen. Regnault's experiments afford some evidence for the belief that the air of the tropics contains slightly less oxygen than that in northern latitudes (v. also Jolly, W. N. F. 61, 520). A similar conclusion has been drawn by Hempel (Ber. 20, 1834) from the analysis of a large number of analyses of air collected simultaneously at Tromsö, Dresden, and Paris. The mean results were:

					Oxygen
Tromsö	.	.	.	.	20·92
Dresden	.	.	.	.	20·90
Paris	.	.	.	.	20·89

From the results of 203 analyses of air collected at five different spots and analysed by three independent methods, it follows that the most probable mean percentage amount of oxygen is 20·93. Numerous determinations by Pettersson and Högland of the air of Stockholm during October, November, and December, 1889, gave O=20·94 (Ber. 22, 3324; Hempel, Ber. 20, 1864; Kreusler, Ber. 20, 991).

Ozone is always present in minute quantity in normal air. Air over marshes contains little or no ozone. No ozone can be detected in the air of large towns or in inhabited houses. Atmospheric ozone is probably formed by the action of electricity on air and on the water contained in it, and by the evaporation of water. No accurate quantitative method is known for the estimation of ozone; all the information we at present possess has been obtained by the use of so-called ozone papers. Of these the best known is Schönbein's, which is based on the fact that ozone liberates iodine from potassium iodide, and thereby renders starch blue. To prepare them, unsized paper is immersed in a solution of 15 parts starch and 1 part potassium iodide in 200 parts of water and dried in the dark. To make a determination of ozone the paper is freely exposed to the air for some hours and moistened with water, and the depth of tint produced compared with a standard scale of colour. The method has no pretensions to scientific accuracy. Houzeau (Ann. Chim. Phys. 4, 27, 5) determines the relative amount of ozone by exposing red litmus paper previously dipped in 1 p.c. sol. of potassium iodide and dried, to the action of the air. The ozone liberates iodine and the free alkali turns the paper blue. Thallium salts are turned brown by the action of ozone, and hence papers soaked in solution of these salts have been used for the recognition of ozone. Paper soaked in a very dilute solution of neutral gold chloride is turned a deep violet colour by ozone (Böttger, Chim. Zentr. 1880, 719).

Attempts have been made to estimate ozone by aspirating large volumes of air through dilute solutions of hydriodic acid and determining the amount of the liberated iodine by iodometric analysis. Also by leading the air through a mixed solution of potassium arsenite and potassium iodide, whereby the liberated iodine converts the arsenite to arsenate. The liquid through which the air had passed was then mixed with a few drops of ammonium carbonate solution and starch paste, and a standard solution of iodine (1 : 1000) added until the blue colour was permanent. A precisely similar experiment was made on equal amounts of distilled water, iodine, arsenite, &c., used, and from the difference in the amount of iodine solution needed the amount of oxidised arsenite and hence the quantity of ozone was determined.

It appears that the amount of ozone varies with the seasons: it is greatest in winter, becomes gradually less during spring and autumn, and is least in summer. Ozone is more frequently observed on rainy days than in fine weather; thunderstorms, gales, and hurricanes are frequently accompanied by relatively strong manifestations of it (cf. Thierry, Compt. rend. 1897, 124, 460).

It is highly probable that many so-called ozone manifestations are due to *hydrogen peroxide*, the existence of which in the air was first demonstrated by Meissner in 1863. Unfortunately, there is no ready mode of discriminating between ozone and hydrogen peroxide. It is probable that the amount of hydrogen peroxide in the air is as a rule greater than that of ozone. Schöne found from observations made at Moscow, that it was invariably present in rain, dew, and snow, and was less in winter than in summer; and more in southerly winds than in those from the north. The amounts in all cases were, however, very minute, the maximum being 1·4 c.c., and the mean 0·38 c.c. hydrogen peroxide vapour in 1000 c.c. air.

The quantity of *aqueous vapour* in the air varies with the temperature: thus 1 cm. of air when saturated with water contains:

At −10°	2·284 grams	At +20°	17·157 grams
0°	4·871	,,	25°	22·843	,,
+ 5°	6·795	,,	30°	30·095	,,
10°	9·362	,,	35°	39·252	,,
15°	12·746	,,		

The most accurate method of determining the amount of aqueous vapour in the air consists in aspirating a given volume of the air through weighed tubes filled with some hygroscopic substance, such as phosphoric oxide or pumice soaked in oil of vitriol and reweighing the tubes, when the increase of weight gives the quantity of moisture present.

Usually, however, the humidity of the air is estimated by means of hygrometers, the best-known form of which is the psychrometer or wet-and-dry-bulb thermometer of August. The *absolute humidity* of the air is the weight of aqueous vapour contained in 1 c.m. The *relative*

humidity denotes the relation between the weight actually present and that which could be theoretically present if the air were saturated ; it is usually expressed in per cent. of the maximum humidity. The air is seldom absolutely saturated with aqueous vapour, although in our moist climate saturation is occasionally very nearly attained. With us the most humid month is December, and the driest is July.

The presence of *carbonic acid* in the atmosphere was first indicated by Black in 1752. The quantity in normal air is about 0·03 p.c. ; in that of large towns it is slightly greater. Angus Smith gives the following summary of results obtained in London in 1864 and 1869 (Air and Rain, 53–58) :—

Over River Thames	. 8 expts.	0·0343 p.c.
In the Park	. 5 ,,	0·0301 ,,
In the streets	. 10 ,,	0·0380 ,,

Any circumstance which interferes with the ready diffusion of the products of respiration and of the combustion of fuel will tend to increase the relative amount of carbonic acid in the air of a town : hence during fogs the amount may be as great as 0·1 p.c.

The amount of carbonic acid in the air of the country at night is usually greater than in the day, as the following comparison shows :—

Air in the day-time.

Observer	Year	Place	Amount
Fr. Schulze .	1861–71	Rostock .	0·0292 p.c.
T. Reiset .	1873–80	Ecorchebœuf	0·0290
G. F. Armstrong	1879	Grasmere	0·0296
Müntz & Aubin .	1881	Vincennes	0·0284
A. Levy .	1877–83	Montsouris	0·0299
Petermann	1892	Gemploux	0·0299
Brown & Escombe	1898–1901	Kew .	0·0294

Air in the night-time.

T. Reiset .	1873–80	Ecorchebœuf	0·0304 p
G. F. Armstrong	1879	Grasmere	0·0330

These differences are mainly due to the exhalation of carbonic acid from plants at night, and, to a smaller extent, to the absence of wind and of any decomposition of the gas by the action of sunlight. Over the sea this diurnal variation is not perceived, as the following results indicate :—

Carbonic acid in sea air.

T. E. Thorpe	Irish Channel and Atlantic Ocean	1865–6	Day . 0·0301 p.c.
			Night 0·0299 ,,
			Mean 0·0300

Comparatively few observations of the amount of carbonic acid in other parts of the earth than Europe have been made. The following may be cited :—

Carbonic acid in the air of tropical countries.

T. E. Thorpe .	S. America .	1866	0·0328 p.c.
Müntz & Aubin	S. and Central America .	1882	0·0278 ,,
		Mean	0·0303

The pressure exerted by the carbonic acid in air is so small that its amount is not perceptibly diminished by rain. The amount also is not sensibly altered in the higher regions of the atmosphere.

Of the several methods which have been proposed for the estimation of atmospheric carbonic acid, the most generally convenient is that of Pettenkofer. It consists in exposing a known volume (say 50 c.c.) of dilute baryta water of known strength to a measured quantity of air (4–6 litres) contained in a well-closed flask. In about 5 or 6 hours the absorption of the carbonic acid will be complete, provided that the sides of the flask have been moistened from time to time by the baryta solution. The baryta solution is then decanted and allowed to stand in a small stoppered bottle until the barium carbonate has settled, when aliquot portions (say 20 c.c.) of the clear solution are withdrawn and the amount of the baryta still in solution determined by titration with a standard solution of sulphuric or hydrochloric acid, of which 1 c.c.=1 mgm. CO_2, phenolthalein being used as indicator (*v.* ACIDIMETRY). The difference in the volume of acid needed for the neutralisation of the baryta before and after exposure to the confined volume of air gives the number of milligrams of carbonic acid contained in the air. Blochmann (Annalen, 237, 72) has described a modification of the apparatus which allows of the titration being effected without exposure to the air of the laboratory.

(For other methods, *v.* Haldane and Pembrey, Roy. Soc. Proc. 1889 ; Cl. Winkler, Chem. Unter. der Industriegase, Freiberg. 1877 ; Reiset, Chem. Soc. Trans. 90, 1114 ; Müntz and Aubin, Compt. rend. 92, 247.)

(For Angus Smith's minimetric method, *v.* Air and Rain ; compare Lunge, Dingl. poly. J. 231, 331.)

(On the influence of the sea upon the amount of atmospheric carbonic acid, *v.* Levy, Ann. Chim. Phys. [3] 34, 5 ; Thorpe, Chem. Soc. Trans. 1867 ; Schloesing, Compt. rend. 93, 1410 ; Lawes, Phil Mag. [5] 11, 206.)

Minute quantities of a m m o n i a and n i t r o u s and n i t r i c a c i d s are also present in the air. Although many of the published observations are probably inaccurate owing to the imperfection of the methods employed, it appears to be proved that the amount of ammonia, which exists mainly as carbonate, is subject to very great variations. By aspirating from 10 to 20 litres of air through Nessler's solution (an alkaline solution of potassium-mercury iodide) and comparing the depth of colour with that produced by a standard solution of an ammonium salt, H. T. Brown (Roy. Soc. Proc. 18, 286) found that the air of Burton-on-Trent during September, October, and November, 1869, taken 2 metres from the ground, contained from 0·4059 to 0·8732 part $(NH_4)_2CO_3$ in 100,000 parts of air, whereas that of the country taken during December and February contained from 0·5102 to 0·6085 part. The direction of the wind had apparently no influence on the amount ; heavy rain seemed to diminish it, but the air was restored to its normal condition in a few hours. Truchot found from 0·93 to 2·79 mgm. per cubic metre in the air of Auvergne, the minimum being found in clear weather and the maximum during fogs (Compt. rend. 77, 1059). Müntz and Aubin, from observations on rain water,

found that the upper strata of air contain much less ammonia than air near the ground. Levy (Compt. rend. 91, 94) found that the rain water and snow of Paris contain in mean 1·17 mgm. of ammoniacal nitrogen per litre of water. The amount of ammonia in this meteoric water is least in winter and greatest during the warmer periods of the year. Gilbert and Lawes found that 1,000,000 pts. of rain water collected in the country contained 0·927 to 1·142 pts. of ammonia. Rain water collected in towns always contains large quantities of ammonia. Thus Angus Smith found that rain water collected in the sparsely populated districts in Scotland contained 0·53 pt. per million, whereas the rain water of London contained 3·45, that of Liverpool 5·38, that of Manchester 6·47, and that of Glasgow 9·1 per million. The increased amount in the towns is doubtless due to the influence of animal life and to the constant presence in greater proportion than in the country of readily decomposable nitrogenous organic matter in the air (cf. Heinrich, Chem. Soc. Abst. 1898, ii. 114).

The quantities of nitrous and nitric acids in the air are even smaller than that of ammonia. Angus Smith (Air and Rain, 287) has given the following results showing the amount contained in a million pts. of rain water :—

Scotland, inland country places	.		0·305
Ireland ,, ,,	.,	.	0·370
Scotland, country places	.	.	0·424
,, towns	.	.	1·164
England, inland country places	.	.	0·749
,, towns	.	.	0·863

Occasionally, and more especially in the air of towns, minute quantities of hydrocarbons, sulphuretted hydrogen, carbonic oxide, sulphurous acid, common salt, alkaline sulphates, are met with. Boracic acid and sal ammoniac have been observed in air in the neighbourhood of active volcanos.

The percentage amount by volume of the inert gases in the air may be stated as follows :—

Argon .	.	.	.	0·93000 p.c.
Krypton	.	.	.	0·00995 ,,
Xenon .	.	.	.	0·00114 ,,
Neon .	.	.	.	0·00123 ,,
Helium	.	.	.	0·00040 ,,

(Moissan, Compt. rend. 137, 600 ; Ramsay, Roy. Soc. Proc. 1908, 80 A, 599.)

Organic matter in greater or less quantity is always present in the air. Much of this is nitrogenous, and apparently readily susceptible to putrefaction, giving rise to products which are alternately transformed into ammonia, nitrous and nitric acids. This form of organic matter reduces silver nitrate and potassium permanganate solutions. A portion of the organic matter consists of micro-organisms which are rapidly deposited in the absence of strong aërial currents. Hesse quantitatively estimates the relative proportions of micro-organisms contained in air by aspirating a given volume of the air through glass tubes coated internally with gelatine peptone, which is then kept at a temperature of about 25° for some days, when the various monad bacilli and micrococci which are arrested and which are capable of growing in the gelatine peptone are recognised by the colonies which they form. By means of this method Percy F. Frankland has made a number of estimations of the micro-organisms contained in the air of towns and in the country and in inhabited buildings. By simultaneously exposing small circular glass dishes partially filled with the nutrient gelatine to the action of the air, a rough estimate was obtained not only of the number of micro-organisms in a given volume of the air, but also of the number which fell during a given time on a definite horizontal area. As the mean of a series of observations made on the roof of the South Kensington Museum between January and June, 1886, it was found that there were 35 organisms in 10 litres of air, whilst 279 was the average number which fell on 1 sq. ft. in 1 minute. Similar experiments made near Reigate and in the vicinity of Norwich showed an average of 14 organisms in 10 litres of air, while 79 fell per sq. ft. per minute. Experiments made in Kensington Gardens, Hyde Park, and on Primrose Hill, gave an average of 24 organisms in 10 litres, and a deposition of 85 per sq. ft. per minute. At St. Paul's Cathedral, 56 organisms were found at the base, 29 in the Stone Gallery, and 11 in the Golden Gallery, in 10 litres of air. At Norwich Cathedral, 18 at the base, 9 at a height of 180 ft. and 7 at 300 ft. In inhabited buildings great variations were observed ; as a rule, the number of micro-organisms was less than was found in the open air when the air of the room was undisturbed, but rose rapidly when the air was set in motion by draughts or by the presence of many people (P. F. Frankland, Roy. Soc. Proc. 40, 509).

Experiments made at the Montsouris Observatory have shown that far fewer organisms are present in the air during winter than during spring and summer. The number also seems to be greatly increased after rain. Whilst in the warm months the number of spores in 1 litre of air was 28, after heavy rain it rose to 95 and 120.

Atmospheric dust is made up of both inorganic and organic matter. Tissandier found that 1 c.m of the air of Paris contained on the average 7·5 mgms. of dust ; after a period of dry weather (8 days), 23·0 mgms., and after heavy rain, only 6·0 mgms. It consisted of from 27 to 34 p.c. volatile matter, and from 66 to 75 p.c. mineral matter, viz. sulphates and chlorides of the alkalis and alkaline earths, oxides of iron, earthy carbonates and phosphates, &c. (cf. J. Aitken, Trans. Roy. Soc. Edin. 35, 37, 39).

RADIOACTIVE CONSTITUENTS OF THE ATMOSPHERE.

A charged electroscope slowly loses its charge in air, and it has been shown that this is not due to moisture, but that, on the contrary, the leakage is greater in dry than in wet weather. The conductivity of air is lessened by passage through a metal tube or by the presence of a weak electric field. These facts indicate that the conductivity of air is due to the presence of charged ions (Townsend, Proc. Roy. Soc. 1899, 65, 192 ; Geitel, Naturw. Rundsch. 21, 221). The rate of leakage of electricity from a charged conductor in dust-free air is the same for positive and negative charges, but varies with the pressure. The loss of charge per second corresponds to the production of about 20 ions

ATOMIC WEIGHTS AND SYMBOLS OF THE ELEMENTS (O=16).

Aluminium	. . . .	Al	27·1	Molybdenum . . . . Mo	96·0
Antimony	. . . .	Sb	120·2	Neodymium . . . . Nd	144·3
Argon .	. . . .	A	39·9	Neon . . . . . Ne	20·2
Arsenic .	. . . .	As	74·96	Nickel . . . . . Ni	58·68
Barium .	. . . .	Ba	137·37	Niton . . . . . Nt	222·4
Bismuth	. . . .	Bi	208·0	Nitrogen . . . . N	14·01
Boron .	. . . .	B	11·0	Osmium . . . . Os	190·9
Bromine	. . . .	Br	79·92	Oxygen . . . . . O	16·00
Cadmium	. . . .	Cd	112·40	Palladium . . . . Pd	106·7
Cæsium .	. . . .	Cs	132·81	Phosphorus . . . . P	31·04
Calcium	. . . .	Ca	40·07	Platinum . . . . Pt	195·2
Carbon .	. . . .	C	12·00	Potassium . . . . K	39·10
Cerium .	. . . .	Ce	140·25	Praseodymium . . . Pr	140·6
Chlorine	. . . .	Cl	35·46	Radium . . . . Ra	226·4
Chromium	. . . .	Cr	52·0	Rhodium . . . . Rh	102·9
Cobalt .	. . . .	Co	58·97	Rubidium . . . . Rb	85·45
Columbium	. . . .	Cb	93·5	Ruthenium . . . . Ru	101·7
Copper .	. . . .	Cu	63·57	Samarium . . . . Sa	150·4
Dysprosium	. . . .	Dy	162·5	Scandium . . . . Sc	44·1
Erbium .	. . . .	Er	167·7	Selenium . . . . Se	79·2
Europium	. . . .	Eu	152·0	Silicon . . . . . Si	28·3
Fluorine	. . . .	F	19·0	Silver . . . . . Ag	107·88
Gadolinium	. . . .	Gd	157·3	Sodium . . . . Na	23·00
Gallium	. . . .	Ga	69·9	Strontium . . . . Sr	87·63
Germanium	. . . .	Ge	72·5	Sulphur . . . . S	32·07
Glucinum	. . . .	Gl	9·1	Tantalum . . . . Ta	181·5
Gold .	. . . .	Au	197·2	Tellurium . . . . Te	127·5
Helium .	. . . .	He	3·99	Terbium . . . . Tb	159·2
Hydrogen	. . . .	H	1·008	Thallium . . . . Tl	204·0
Indium .	. . . .	In	114·8	Thorium . . . . Th	232·4
Iodine .	. . . .	I	126·92	Thulium . . . . Tm	168·5
Iridium .	. . . .	Ir	193·1	Tin . . . . . Sn	119·0
Iron .	. . . .	Fe	55·84	Titanium . . . . Ti	48·1
Krypton	. . . .	Kr	82·9	Tungsten . . . . W	184·0
Lanthanum	. . . .	La	139·0	Uranium . . . . U	238·5
Lead .	. . . .	Pb	207·10	Vanadium V	51·0
Lithium	. . . .	Li	6·94	Xenon . . . . . Xe	130·2
Lutecium	. . . .	Lu	174·0	Ytterbium (Neoytterbium) . Yb	172·0
Magnesium	. . . .	Mg	24·32	Yttrium . . . . Yt	89·0
Manganese	. . . .	Mn	54·93	Zinc . . . . . Zn	65·37
Mercury	. . . .	Hg	200·6	Zirconium . . . . Zr	90·6

of either sign in each cubic centimetre of air
(Wilson, Proc. Roy. Soc. 68, 151).

Elster and Geitel have shown (Wied. Ann.
[2] 39, 321) that ions are produced during
the formation of ozone by contact of air with
flames or by the slow oxidation of phosphorus,
&c., but the mere presence of ozone does not
impart conductivity to air (Jorissen and Ringer,
Ber. 1906, 39, 2090). Langevin (Compt. rend.
1905, 140, 232) states that in air, in addition to
ordinary ions carrying charges equal to that of a
hydrogen ion in solution, there exist other ions
having a much smaller mobility, but carrying
charges fifty times as great.

Nordmann has described (Compt. rend. 140,
430) an apparatus for continuously recording the
state of ionisation of the air. Air is caused to
circulate between the plates of a cylindrical
condenser, and the charge given up by the ions
is removed by dropping water. The condenser
is connected with an electroscope, the deviations
of which are recorded photographically, and are
proportional to the number of ions present in
unit volume of air. Another apparatus for the
same purpose is that of Langevin and Moulin
(Compt. rend. 140, 305).

No satisfactory explanation of the ionisation
of air was found until Elster and Geitel showed
(Physikal. Zeitsch. 1901, 76, 590) that a negatively
charged wire suspended in the open air became
coated with radioactive matter, the presence of
which could be proved by its action upon a
charged electroscope, although the quantity
present was altogether too small to respond to
any chemical test. Rutherford and Allan
confirmed this observation, and measured the
rate of decay of the deposit (Phil. Mag. 1902,
vi. 4, 704). Later, Allan showed that the
radioactive matter could be removed from the
wire by rubbing it with a piece of felt or by
solution in ammonia, and that the ashes of the
felt or the residue from the evaporation of the
solution showed radioactivity having a period
of decay equal to that of the deposit on the
wire (Phil. Mag. 1904, vi. 7, 140).

These phenomena are due to the presence
in the atmosphere of the gaseous emanations
of radioactive elements, probably those of
radium and thorium (Bumstead, Amer. J. Sci.
1904, 18, 1). The amount of active matter
is not constant, but increases with increased
circulation of the air, and is therefore probably
due to the presence of radium in the soil (Simp-
son, Phil. Trans. 1905, A, 205, 61). Balloon
observations made by Flemming (Zeitsch.
physikal. Chem. 1908, 9, 801; show that radium
emanation is present even at a height of 3000
metres. Thorium emanation exists principally
in air taken from the soil or the lower layers
of the atmosphere (Gockel and Wulf, Physikal.
Zeitsch. 1908, 9, 907). That it is not widely
disseminated in the air is probably due to its
rapid rate of decay (Blanc, Physikal. Zeitsch.
1908, 9, 294). The experiments of Dadourian
(Physikal. Zeitsch. 1908, 9, 333) and of Wilson
(Phil. Mag. 1909, 17, 321) indicate that air
normally contains about 3700 times as much
radium emanation as thorium emanation.

By passing air through a copper spiral cooled
in liquid air, the emanations are condensed, and
may then be volatilised into an electroscope and
the amount estimated by their effect in ionising
VOL. I.—T.

the contained air. Ashman (Amer. J. Sci.
1908, 26, 119) has thus found in Chicago air
an amount of emanation per cubic metre equal
to that which would be in equilibrium with
about 1.0×10^{-10} gram of radium. By absorb-
ing the emanations in charcoal and then
volatilising them into an electroscope, Eve
has obtained results of the same order—
0.8×10^{-10} gram for the radium equivalent of
the emanation in the air of Montreal (Phil. Mag.
1907, 14, 724), and has shown by numerous
observations that the value is not affected by
temperature, but that a deep cyclone with rain
causes an increase, whilst anti-cyclonic conditions
cause a decrease in the amount of emanation
(Phil. Mag. 1908, 16, 622). These results have
been confirmed by Satterly (Phil. Mag. 16, 584).

All investigators are agreed that these
emanations are the chief cause of the ionisation
of air, but Wilson, by experiments on the effect
of pressure on 'natural' ionisation of air enclosed
in a metal cylinder, has shown (Phil. Mag. 1909,
17, 216) that it is partly due to some pene-
trating radiation the source of which is not
in the soil (Pacini, Atti R. Acad. Lincei, 1909,
18, 123). Both Pacini and Wulf (Physikal.
Zeitsch. 1909, 10, 152) have detected a double
diurnal periodicity in the state of ionisation of
the air.

(See also Harvey (Physikal. Zeitsch. 1909,
10, 46) and Runge (Chem. Soc. Abstr. 1908, ii.
80).)

ATOXYL. Trade name for the mono-sodium
salt of p-aminophenylarsinic acid (Ehrlich
and Bertheim). Forms a white crystalline taste-
less, odourless powder. So named from its
relatively low toxic action (v. ARSENIC, ORGANIC
COMPOUNDS OF).

ATRAMENTUM STONE. (Atramentumstein,
Ger.) A product of the partial oxidation
of iron pyrites, consisting of a mixture of ferrous
and ferric sulphates with free ferric oxide. Used
in the manufacture of ink.

ATRANORIN $C_{19}H_{18}O_8$ is present in the
lichens Evernia vulpina, E. prunastri, E. fur-
furacea, Lecanora atra, L. sordida, Parmelia
perlata, P. physodes, Physcia stellaris, Xanthoria
parietina, Cladonia rangiformis, and Stereocaulon
vesuvianum. It forms colourless prisms; m.p.
195°–197° (Zopf), 187°–188° (Hesse); easily
soluble in hot chloroform, soluble in alkalis with
a yellow colour.

According to Paternò, by heating with water
to 150°, atranorin gives physciol (methyl-phloro-
glucinol), and atraric acid (betorcinol carboxylic
acid methyl ester), and these substances are also
obtained when atranorin is heated with acetic
acid in a sealed tube (Hesse).

Physciol forms colourless needles, m.p. 104°–
105°, gives with ferric chloride a blue-green
colouration, and possesses, according to Hesse,
the constitution of a methylphloroglucinol
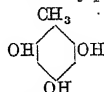
Betorcinol carboxylic acid methyl ether
$C_{10}H_{12}O_4$, crystallises in leaflets, m.p. 140°–141°;
and gives with calcium hypochlorite solution a
blood-red colouration. Digested with boiling

z

hydriodic acid, it is converted into *β-orcin* (Stenhouse and Groves) $C_8H_{10}O_2$, according to the equation :—

$$C_{10}H_{12}O_4 + HI = CH_3I + CO_2 + C_8H_{10}O_2.$$
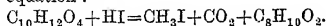
β-Orcin (*see* also *Barbatic acid*) is 1·4-dimethylresorcin.

The constitution assigned to betorcinol carboxylic acid methyl ether is :—
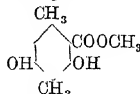
Heated with alcohol in a sealed tube, atranorin gives, according to Paternò, *Hæmatommic acid* and *Hæmatomminic acid* ; but the researches of Hesse indicate that these compounds in reality consist of *hæmatommic acid methyl ether* and *betorcinol carboxylic acid methyl ether*.

Hæmatommic acid methyl ether $C_{10}H_{10}O_5$ forms colourless needles, m.p. 147°, soluble in alkaline solutions with a yellow colour. With ferric chloride it gives a purple-red or purplebrown colouration. The *ethyl ether*, $C_{11}H_{12}O_5$, gives colourless needles, melts at 111°–112° (Hesse); 113°–114° (Zopf). It is represented by the formula :—
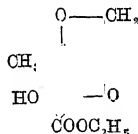
When a solution of atranorin in dilute acetic acid is gently evaporated, *atranorinic acid* (Hesse) is produced. This compound is also present in the *Cladonia rangiformis* (Hesse) when gathered in December, but is absent from this lichen in summer.

Atranorinic acid $C_{18}H_{18}O_9,H_2O$ forms colourless crystals, which are anhydrous at 100°, and then melt at 157°. With ferric chloride it gives a dark brownish-red colouration. Heated with hydriodic acid it gives *β-orcin*, or with alcohol yields carbon dioxide, *physciol* and *β-orcin*. The constitutions assigned to atranorinic acid (I.) and atranorin itself (II.) are as follows :—

I.   II.
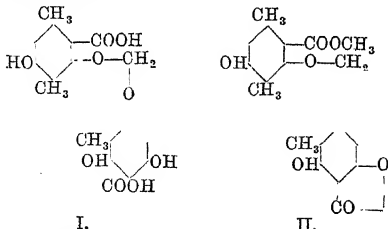
References.—Paternò and Oglialaro (Gazz. chim. ital. 7, 289), Paternò (*ibid.* 10, 157 and 12, 257); Zopf (Annalen, 288, 38); Hesse (J. pr. Chem. 57, 280); Lüdecke (Annalen, 288, 42); Hesse (Annalen, 119, 365); Stenhouse and Groves (Annalen, 203, 302).   A. G. P.

ATROLACTINIC ACID *v.* LACTIC ACID.

ATROPINE *v.* VEGETO-ALKALOIDS.

ATTAR OF ROSES *v.* OILS, ESSENTIAL.

AUCUBIN *v.* GLUCOSIDES.

AURAMINE. *Iminotetramethyldiparamino-diphenylmethane hydrochloride*, $C_{17}H_{21}N_3,HCl,H_2O$; $NMe_2 \cdot C_6H_4C(NH) \cdot C_6H_4 \cdot NMe_2,HCl,H_2O$ (Graebe), or $Me_2N \cdot C_6H_4 \cdot C(NH_2) : C_6H_4 : NMe_2Cl,H_2O$ (Stock; Dimroth and Zoeppritz). According to Stock (J. pr. Chem. 47, 401; Ber. 1900, 33, 318), and Dimroth and Zoeppritz (Ber. 1902, 35, 984), the base has the constitution assigned to it by Graebe (Ber. 1899, 32, 1678; 1902, 35, 2615), but the hydrochloride and the other salts have the quinonoid structure $Me_2N \cdot C_6H_4 \cdot C(NH_2)$: $C_6H_4 : NMe_2Cl$, and are to be regarded as derivatives of triphenylmethane in which an amino- group has replaced one of the benzene residues.

Auramine, the first member of a series of yellow, orange-yellow, or brown dyes, is the hydrochloride of a colourless base obtained by the action of ammonia on tetramethyldiamino-benzophenone, and comes into the market either in the nearly pure form as *Auramine O*, or mixed with dextrin as *Auramine I.* and *II.* (Graebe, Ber. 20, 3264). Fehrmann (Ber. 20, 2847) proposed to restrict the name auramine to the colourless base, but such a change would inevitably lead to confusion ; and Graebe (*l.c.*) has consequently adopted the name *auramine-base* for the base itself, using the term auramine in its usual signification.

Preparation.—(1) Auramine was originally prepared from tetramethyldiaminobenzophenone by dissolving it in some indifferent solvent such as chloroform, carbon disulphide, hydrocarbons, &c., treating it with half its weight of phosphorus trichloride or oxychloride, and adding excess of concentrated ammonia to the chlorinated compound thus obtained (B. A. S. F., D. R. P. 27789).

(2) Auramine can be prepared more economically by heating tetramethyldiaminobenzophenone with suitable ammonium salts, such as the chloride, acetate, tartrate, thiocyanate, &c., in the presence of zinc chloride at 200° (B. A. S. F., D. R. P. 29060). Acetamide may be employed instead of ammonium salts (B. A. S. F., D. R. P. 38433), or the dye may be obtained by heating aniline hydrochloride with zinc chloride and carbamide, phenylcarbamide, diphenylcarbamide, or carbanil (Ewer and Pick, D. R. P. 31936); but these alternative methods have no practical importance.

(3) At the present day, auramine is prepared by a method due to Sandmeyer (Eng. Pat. 12549, 1889 ; 16666, 1890) and Walker (J. Soc. Chem. Ind. 1901, 34), which consists in heating a mixture of tetramethyldiamino-diphenylmethane, sulphur, ammonium chloride, and sodium chloride in a current of dry ammonia. A modification of this method is described by J. Y. Johnson (B. A. S. F., D. R. P. 71320; Eng. Pat. 6249, March 23, 1893), in which the tetramethyldiaminodiphenylmethane is replaced by dimethyl - tetramethyldiaminodiphenylmethane obtained by condensing acetone and dimethylaniline (Ber. 1878, 12, 813). About 14 kilos. of dimethyl-tetramethyldiaminodiphenylmethane are mixed with 120 kilos. of salt, 6 kilos. of sulphur, and 7 kilos. of ammonium chloride, and a stream of ammonia gas is passed through the mixture for eight hours at 175°.

The mass is first washed with cold water to dissolve away the salt and ammonium chloride, it is then dissolved in water at 70°, filtered, and the dye salted out, pressed, and dried. Auramine is also prepared by heating dimethylaminobenzamide and dimethylaniline with zinc chloride at 160°–200° (D. R. P. 77329).

(4) Guyot (Compt. rend. 1907, 144, 1219; J. Soc. Chem. Ind. 1908, 679) has synthesised auramines by means of the oxalic esters. Tetraalkyldiaminodiphenylglycollic esters (J. Soc. Chem. Ind. 1907, 603) form neutral salts with acids, the indigo-blue aqueous solutions of which react with ammonia even when dilute to furnish tetraalkyldiaminodiphenylamino acetic esters, according to the equation:

$$(R_2N\cdot C_6H_4)_2CCl\cdot CO_2R' + 2NH_3$$
$$= NH_4Cl + (R_2N\cdot C_6H_4)_2C(NH_2)CO_2R'.$$
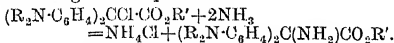
These new compounds are exo-carboxylic derivatives of the leucauramines, and possess all the properties of the latter. They dissolve in glacial acetic acid with an intense blue coloration, and condense with aromatic tertiary amines to form triphenylmethane derivatives. Thus ethylhexamethyltriaminotriphenyl acetate is produced by heating an equimolecular mixture of dimethylaniline and ethyltetramethyldiaminodiphenylaminoacetate in glacial acetic acid on the water-bath for some minutes:

$$(Me_2N\cdot C_6H_4)_2C(CO_2Et)\cdot NH_3 + C_6H_5\cdot NMe_2$$
$$= (Me_2N\cdot C_6H_4)_2C(CO_2Et)C_6H_4NMe_2 + NH_3.$$
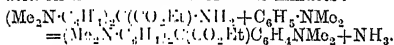
When a dilute alkaline solution of the aminoacetic ester is oxidised with dilute potassium ferricyanide solution in the cold, a quantitative yield of the corresponding auramine is produced.

Properties.—Auramine crystallises from water in yellow scales, which seem to consist of six-sided tables, and from alcohol in golden-yellow scales, melts at 267° (Graebe), carbonises at 265°–280° without previous fusion (Fehrmann), and is sparingly soluble in cold but readily soluble in hot water; the temperature of the aqueous solution, however, must not exceed 60°–70°, otherwise decomposition ensues, with the formation of ammonia and tetramethyldiaminobenzophenone. On treatment with mineral acids, the aqueous solution undergoes a similar decomposition either slowly in the cold or very rapidly on heating. Spectroscopically, auramine behaves like most yellow dyes; a hot concentrated aqueous solution, however, shows two bands, one in the red and one in the green, which become broader on dilution and finally coalesce, forming a bright broad band extending from the middle of the red to the commencement of the green (Graebe). On treatment in the cold with ammonia, auramine (crystallised from alcohol) is converted into the colourless base $C_{17}H_{21}N_3$, which melts at 136°, and is characterised by yielding with acids intensely yellow, and for the most part crystalline salts, which dissolve in water and alcohol without fluorescence. Alkaline reducing agents, such as sodium amalgam, slowly decolourise the alcoholic solution of auramine, forming *leucauramine* $C_{17}H_{23}N_3$, a colourless crystalline reduction compound melting at 135°, which dissolves in acetic acid with an intense blue colour owing to its decomposition into ammonia and tetramethyldiaminobenzhydrol.

Auramine dyes wool and silk direct, pro-

ducing colours which are pure yellow and fairly fast to light and soap. Cotton, for which the dye is chiefly used, requires to be first mordanted with tannin and tartar emetic, and on this account auramine is useful for producing compound shades with other basic colouring matters, such as safranine, benzaldehyde-green, &c., which are fixed by the same mordant. (For further information v. Köchlin, Wagner's Jahr. 1884, 1139.)

Salts. *Auramine hydrochloride* $C_{17}H_{21}N_3$, HCl, is sparingly soluble in water, and has $\mu\infty$ 90·4 at 25°; the *palmitate* $C_{17}H_{21}N_3, C_{16}H_{32}O_2$, has m.p. 57°, the *stearate* has m.p. 68° (Gnehm, Röteli Zeit. Angew. Chem. 1898, 487); the *methyl sulphate* obtained by the action of dimethyl sulphate on auramine, has m.p. 225° (Zohlen, J. pr. Chem. 1902, 66, [20] 387).

Substituted Auramines. In addition to auramine, substituted auramines have also been prepared. **Auramine G,** obtained by treating in a hot mixture of *sym*-dimethyldiamino-di-o-tolylmethane (from methyl o-toluidine and formaldehyde) sulphur, ammonium chloride and salt with dry ammonia gas (Gnehm and Wright, U.S. Pat. 488430), has m.p. 120°, the *picrate* has m.p. 234°, the *sulphate* m.p. 182°, the *oxalate* m.p. 210°. *Leucauramine G* has m.p. 208°.

Metaxylylauramine can be obtained by heating an intimate mixture of 10 kilos. of tetramethyldiaminobenzophenone and 23 kilos. of metaxylidine hydrochloride for about 4 hours at 200° in an enamelled vessel provided with a mechanical stirrer. Fusion takes place slowly, and the mass becomes reddish yellow in colour, assuming finally a greenish metallic lustre towards the close of the reaction, which is complete when a test specimen is almost entirely soluble in water. The cooled mass is extracted with hot water, and the dye precipitated in orange-yellow flocks by addition of sodium nitrate to the filtered solution.

Methylauramine MeN : $C(C_6H_4\cdot NMe_2)_2$, m.p. 133° (Zohlen, J. pr. Chem. 1902, 66, 387), the *hydrochloride* $C_{18}H_{24}N_3Cl$, has m.p. 225°, the *platinichloride* $(C_{18}H_{24}N_3Cl)_2PtCl_6$, m.p. 190°–200°, the *hydrobromide* $C_{18}H_{24}N_3Br$, m.p. 260°, the *hydriodide* $C_{18}H_{34}N_3I$, m.p. 259°, forms a series of unstable polyiodides: the *trichromate* $(C_{18}H_{24}N_3)_2Cr_3O_{10}$, m.p. 70°, the *thiocyanate* $C_{18}H_{24}N_3CNS$, m.p. 213°–214°, and the *picrate* $C_{18}H_{23}N_3, C_6H_3O_7N_3$, m.p. 225°.

Ethylauramine EtN : $C(C_6H_4\cdot NMe_2)_2$, from auramine ethyl iodide and zinc oxide (D. R. P. 136616), m.p. 130°–131°, dyes mordanted cotton a pure yellow.

Phenylauramine PhN : $C(C_6H_4\cdot NMe_2)_2$, prepared by heating tetramethyldiaminodiphenylmethane with aniline and sulphur at 200° (Feer, D. R. P. 53614); or by heating dimethylaminobenzanilide with dimethylaniline and phosphorus oxychloride (D. R. P. 44077); has m.p. 172°; the *hydriodide* $C_{23}H_{25}N_3, HI$, has m.p. 242°; the *methiodide* $C_{23}H_{25}N_3, MeI$, has m.p. 214°.

Paraminophenylauramine $NH_2 \cdot C_6H_4N$: $C(C_6H_4\cdot NMe_2)_2$ (Finckh and Schwimmer, J. pr. Chem. 1894, 50, 401), has m.p. 221°–222°; the *hydrochloride,* m.p. 224°; the *picrate,* m.p. 185°–186° (corr.); the *diacetyl* derivative has m.p. 194°–195°; the *triacetyl* derivative has m.p. 257°–258°; *monobenzoyl* derivative has m.p. 117°; and the *dibenzoyl* derivative has m.p. 180°–181°;

paraphenylenediauramine $C_6H_4[N:C(C_6H_4\cdot NMe_2)_2]_2$, has m.p. 311°–312°.

Orthaminophenylauramine, m.p. 199°–200°, forms a *picrate*, m.p. 220°–221°, and a *benzoyl* derivative, m.p. 236°–237°; *orthophenylene-diauramine* has m.p. 305°.

p-**Tolylauramine**, obtained by heating te-tramethyldiaminodiphenylmethane with *p*-toluidine and sulphur (D. R. P. 53614), or from dimethylaminobenzo - *p* - toluidine, dimethyl-aniline, and phosphorus oxychloride (D. R. P. 44077), has m.p. 178°. *o*-**Tolylauramine** similarly prepared to the *p*- compound has m.p. 173°–174°, α - **naphthylauramine** $(Me_2N\cdot C_6H_4)_2C:NC_{10}H_7$ (D. R. P. 44077), has m.p. 225°. β-**naphthyl-auramine** $(Me_2N\cdot C_6H_4)_2C:N\cdot C_{10}H_7$ (D. R. P. 44077), m.p. 179° – 180°. **Benzylauramine** $C_6H_5\cdot CH_2\cdot N:C(C_6H_4\cdot NMe_2)_2$ (D. R. P. 136616) from auramine benzylchloride and magnesia, has m.p. 116°. **Benzoylauramine** (Finckh and Schwimmer, J. pr. Chem. 1894, 50, 401) NBz : $C(C_6H_4\cdot NMe_2)_2$, has m.p. 179° (corr.).

Methylphenylauramine hydrochloride, *de-phenylauramine*, and *pentamethyleneauramine* have been described by Stock (Ber. 1900, 33, 318 ; J. pr. Chem. 47, 401–413). The following compounds, closely related to the naphthylauramines, form the subject of a patent (D. R. P. 44077) : *tetraethyldiaminodiphenylmethylene - α - naphthyl-amine* $(Et_2N\cdot C_6H_4)_2C:N\cdot C_{10}H_7$, m.p. 157°–158° ; *dimethyldiethyldiaminodiphenylmethylene-α-naphthylamine* $(Me_2N\cdot C_6H_4)(Et_2N\cdot C_6H_4)C:N\cdot C_{10}H_7$, m.p. 177°–178° ; *tetraethyldiaminodi-phenylmethylene-β-naphthylamine* $(Et_2N\cdot C_6H_4)_2C:N\cdot C_{10}H_7$, m.p. 155° ; *dimethyldiethyldiaminodi-phenylmethylene-β-naphthylamine* $(Me_2N\cdot C_6H_4)(Et_2N\cdot C_6H_4)C:N\cdot C_{10}H_7$, m.p. 163°–164°.

The substituted auramines dye silk and wool, and also cotton after mordanting with tannin. The shades produced on cotton are, however, distinctly reddish or brownish-yellow compared with the pure yellow produced by auramine itself ; for example, the auramines from orthotoluidine, metaxylidine and cumi-dine hydrochlorides dye cotton golden-yellow ; those from aniline and paratoluidine dye orange-red, that from metaphenylenediamine dyes orange-brown, and those from α- and β-naphthyl-amine dye brownish-yellow shades (B. A. S. F., D. R. P. 29060 ; Fehrmann, Ber. 20, 2852).

AURANTIA (*Kaisergelb*) is the commercial name of the ammonium salt of hexanitro-diphenylamine.

Hexanitrodiphenylamine $NH\cdot C_6H_2(NO_2)_3]_2$ is obtained by treating diphenylamine or methyldi-phenylamine with nitric acid, and, after the first vigorous action has subsided, heating to com-plete the reaction. The product is then ex-tracted with water to remove any resin or picric acid associated with it, and finally crystallised from acetic acid.

It forms bright-yellow prisms, melts at 238° with decomposition, but can be sublimed in yellow needles by careful heating, and is almost insoluble in water, more soluble in alcohol, and easily soluble in ether. It readily yields salts, and the *ammonium* salt (aurantia) crystallises in lustrous brown-red needles, although com-mercially it is obtained as a brick-red powder which dissolves in water and dyes silk and wool a beautiful orange colour (Gnehm, Ber. 7, 1399 ; 9, 1245 ; *cf.* Townsend, Ber. 7, 1249 ; Mertens,

Ber. 11, 845). Aurantia is used chiefly as a dye for leather (W. J. 1877, 1002). Like hexanitro-diphenylamine, it is very explosive, but any danger may be avoided by moistening it with glycerol (W. J. 1876, 996). According to Gnehm (Ber. 9, 1246, 1557) and Bayer & Co. (W. J. 1877, 879), aurantia produces skin eruptions ; Martius, however, contends that this effect is due to idiosyncrasy, and quotes the opinions of Salkowski and Ziureck in support of his statement (Ber. 9, 1247), and the question appears to have received a solution in this sense in Germany, since the ministerial order of November 8, 1877, prohibiting its manufacture, was cancelled in June, 1880.

AURIN and **ROSOLIC ACID.**

History.—Rosolic acid was first discovered and its tinctorial properties described by Runge (P. 31, 65), who obtained it from coal-tar oil by dissolving the residue from the distillation of phenol in alcohol, adding milk of lime, filtering off the brown precipitate of calcium brunolate and precipitating the red solution of calcium rosolate with acetic acid. Later, Tschelnitz (J. pr. Chem. 71, 416) and Müller (Chem. Soc. Trans. 11, 1) found that the yield was greater if the product after addition of the lime was heated in the air for some time, whilst Smith (J. 1857, 448) and Jourdin (J. 1861, 943) showed that crude phenol was converted into rosolic acid by heating it with soda and manganese dioxide or mercuric oxide. Kolbe and Schmitt (Annalen, 119, 169) and, simultaneously, Persoz (Fr. Pat. 54910, July 21, 1861) obtained it by heating phenol and oxalic acid with sulphuric acid, and this method was adopted for preparing the acid on the large scale by Wurtz (Schmidt, Dingl. poly. J. 166, 318) who termed it (yellow) corallin (known commercially as aurin in England), and by Guinon, Marnas and Bonnet (Dingl. poly. J. 167, 390), who converted it into pæonin or red corallin by digestion with aqueous ammonia at 150°. The reaction was further investigated by Fresenius (J. pr. Chem. [2] 5, 184), by Prud'homme (Zeitsch. angew. Chem. [2] 19, 359), and by Comaille (Compt. rend. 77, 678), the last of whom found that the proportion of oxalic acid used was too large. By diazotising rosaniline, Caro and Wanklyn (Chem. News, 14, 37 ; Proc. Roy. Soc. 15, 210) obtained rosolic acid $C_{20}H_{16}O_3$, which, however, was not identical with the pro-duct from phenol. Caro (Phil. Mag. [4] 32, 126), moreover, showed that the formation of rosolic acid from phenol is dependent on the presence of cresol or of some simple (methane) derivative of the fatty series of organic compounds (com-pare Guareschi, Ber. 5, 1055 ; Zulkowsky, Anna-len, 194, 122). The nature and composition of the products obtained in Kolbe and Schmitt's reaction were not, however, accurately known until 1878, when the researches of Dale and Schorlemmer (Annalen, 166, 279 ; 196, 75), Caro and Graebe (Annalen, 179, 184 ; Ber. 11, 1116, 1348), E. and O. Fischer (Ber. 11, 473) and Zulkowsky (Annalen, 194, 122 ; 202, 179) established the fact that the action of oxidising agents on a mixture of phenol and cresol, or of oxalic acid on phenol, results in the formation of a mixture of red colouring matters (corallin) con-taining two well-characterised substances termed aurin $C_{19}H_{14}O_3$, and methylaurin $C_{20}H_{16}O_3$. Aurin is the lower homologue of Caro and

Wanklyn's rosolic acid, and is sometimes known as pararosolic acid, since it can be obtained by diazotising pararosaniline (E. and O. Fischer, Annalen, 194, 268).

Corallin. This name is applied to the red colouring matter obtained by heating phenol and oxalic acid with sulphuric acid. According to Zulkowsky (Annalen, 194, 122 ; 202, 134; Monatsh. 16, 363), a mixture of pure phenol (10 parts) and sulphuric acid of. 66° B. (5 parts) is heated with anhydrous oxalic acid (6 parts) added in three equal quantities, at 120°–130° until the mass becomes viscid and the evolution of gas (a mixture of CO and CO_2 in equal volumes) slight. This stage is reached in about 24 hours, and the product is then poured into so much water that the further addition of water does not produce a precipitate. The corallin is thus separated from phenolsulphonic acid and unattacked phenol, and the yield by this process amounts to 60–70 p.c. Corallin has been shown to be a mixture of pseudo-rosolic acid or corallin-phthalin (70 p.c.), to which it owes its resinous consistency, with aurin, methylaurin, and, according to Zulkowsky, with several other products, of which very little is known.

Properties.—It is a brittle resinous substance with a green metallic lustre, and yields a red powder. It has been employed as a dye for silk and wool (Schröder, Dingl. poly. J. 204, 397), and used for printing on cotton, silk, and wool. In printing with corallin, any acids with which it may come in contact during the process must be neutralised, otherwise a yellow instead of a turkey-red colour is the result. Kielmeyer recommends magnesia for this purpose (Wagner's Jahr. 1872. 709).

The following substances have been isolated from corallin :—

(1) **Aurin** (*pararosolic acid*) $C_{19}H_{14}O_3$ or $C(C_6H_4 \cdot OH)_2 : C_6H_4 : O$. The formation of the aurin present in corallin has been attributed to the reaction :

$$3C_6H_6O + H_2C_2O_4 = C_{19}H_{14}O_3 + H_2CO_2 + 2H_2O$$
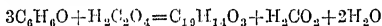
(D. and S. Annalen, 196, 79 ; compare, however, Zulkowsky, Annalen, 202, 184 ; E. and O. Fischer, Ber. 11, 201 ; Gukassianz, Ber. 11, 1179 ; Z. Ber. 11, 1431 ; Neneki and Schmid, J. pr. Chem. [2] 25, 273) : Z. Monatsh. 5, 108 ; Staub and Smith, Ber. 17, 1740).

Preparation.—Aurin can be obtained by diazotising pararosaniline (E. and O. Fischer, *l.c.* ; compare ROSOLIC ACID), but the process has no practical value. It can be obtained pure and in good yield (95 p.c. when zinc chloride is used) by heating phenol (14 parts) with carbon tetrachloride (8 parts) and zinc chloride (30 parts), or aluminium chloride (10 parts), or stannic or ferric chloride (20–30 parts) at 140°–160° in an autoclave during 4 hours with occasional stirring. The product, when cold, is purified by driving off unattacked phenol with steam, and removing soluble impurities by extraction with water (Heumann, D. R. P. 68976 of April 3, 1892, expired Aug. 1893; compare Friedel, Bull. Soc. chim. 50, 2). Elbs substitutes chloropicrin for carbon tetrachloride, heating the mixture for one to two days in a steam-bath, but does not state the yield (Ber. 16, 1275).

Reference has been made to Smith's and Jourdin's methods of oxidising crude phenol.

Rudolph (Zeitsch. angew. Chem. 19, 384) heats paracresol (108 grams) and phenol (188 grams) dissolved in 32 p.c. caustic soda solution (400 grams) with sodium dichromate (300 grams) also dissolved in 32 p.c. caustic soda solution (250 grams) for some hours at 180° under pressure. The aurin is purified by conversion into the compound with sodium bisulphite.

Another process is that described by N. Caro (Ber. 25, 948), in which a mixture of dihydroxy-diphenylmethane and phenol in mol. prop. is oxidised by a cold solution of sodium nitrite in concentrated sulphuric acid.

To obtain aurin from the commercial product, Dale and Schorlemmer (Annalen, 166, 280) treat a concentrated alcoholic solution of corallin with gaseous ammonia until crystals of the compound of aurin with ammonia cease to form ; the precipitate is then heated with hydrochloric acid or acetic acid to remove ammonia, and the product repeatedly crystallised from alcohol. A second method, in which the commercial product is washed with cold alcohol and the residue repeatedly crystallised from alcohol, has also been described (D. and S. Annalen, 196, 77). A third method, due to Zulkowsky (Annalen, 202, 185), in which a solution of corallin in dilute soda ley is saturated with sulphur dioxide, and the resinous pseudo-rosolic acid or corallin-phthalin precipitated by water, has been described. The separation of the aurin from the methylaurin, and leucorosolic acid left in solution, is effected by the aid of sulphur dioxide, with which aurin forms a crystalline compound. The process can be varied by dissolving corallin in a 1·25 p.c. solution of caustic soda, precipitating the clear solution by carbon dioxide, suspending the precipitate in water acidified with acetic acid, and washing it finally with water. The precipitate (1 part) is then dissolved in boiling alcohol (20 parts), and the aurin separated by adding to the solution one-fourth its volume of boiling water (Monatsh. 16, 363). The yield of aurin by any of these methods amounts to less than 10 p.c.

Properties.—Aurin crystallises in garnet-red rhombic forms, which appear rose-red by transmitted, and show a sky-blue lustre by reflected, light ; it does not melt at 220°. In alcohol and acetic acid it dissolves, forming yellow-red, and in alkalis and ammonia carmine, solutions. Aurin combines with sulphur dioxide, forming the compound $H_2SO_3 \cdot 2C_{19}H_{14}O_3 + 4H_2O$, which crystallises in red cubes and cubic octahedra, showing a green metallic lustre (D. and S. Annalen, 166, 184 ; Z. Annalen, 202, 206) ; it also combines with alkaline bisulphites (D. and S.). Acetic anhydride converts it into two *triacetyl*- compounds, $C_{19}H_{13}O_4(C_2H_3O)_3$, m.p. 171°–172° and 146°–149°, from each of which aurin can be regenerated by hydrolysis (Herzig and Smoluchowski, Monatsh. 15, 73 ; Herzig, *ibid.* 17, 191). Bromine reacts with it in acetic acid solution to form *tetrabromaurin* $C_{19}H_{10}O_3Br_4$, which yields violet solutions with alkalis, and in acid solution is a dark-violet dye for silk and wool (D. and S. Annalen, 196, 81 ; compare Z. Monatsh. 3, 465 ; Ackermann, Ber. 17, 1624). With iodine in alkaline solution, or electrolytically with potassium iodide and an alkali, aurin yields a *triiodo*- derivative $C_{19}H_{11}O_3I_3$, for which some pharmaceutical value is claimed (Classen, D. R. P. 85929, of

May 27, 1894). *Tetranitroaurin* $C_{19}H_{10}O_3(NO_2)_4$, m.p. 140°, and several ethyl ethers have been prepared by Ackermann (*l.c.*; for *aurindimethyl ether* $C_{19}H_{12}O(OCH_3)_2$, see Herzig, Monatsh. 29, 653). When an alcoholic solution of aurin is saturated with ammonia, *aurin-ammonia* $C_{19}H_{14}O_3$,(NH$_3$)$_3$ is obtained ; this crystallises in dark-red needles, and rapidly loses ammonia on exposure to air. If, however, aurin is heated with aqueous or alcoholic ammonia at 180°–200° for 20 hours, it yields paraleucaniline (D. and S. Annalen, 196, 75) ; and similar treatment with methylamine and aniline results in the formation of trimethyl- and triphenyl- rosaniline respectively. Reducing agents, and zinc-dust with acetic acid in particular, convert it into *paraleucaurin* $CH(C_6H_4 \cdot OH)_3$, which crystallises from alcohol in colourless lustrous needles, does not melt at 130°, yields a *triacetyl-* derivative, melting at 138°–139°, and on oxidation with permanganate or ferricyanide of potassium, does not yield aurin, but an undetermined red product (Dale and Schorlemmer; Zulkowski; Caro and Graebe, *l.c.*).

The following hydroxyaurins have been prepared by Nencki (J. pr. Chem. [2] 25, 275): cresolaurin $C_{22}H_{20}O_3$; resaurin $C_{19}H_{14}O_6$; and orcinolaurin, $C_{22}H_{18}O_5$.

Other hydroxyaurins, and several aurin-carboxylic acids have been made by N. Caro's process (*l.c.*, Ber. 25, 2671 ; J. R. Geigy and Co., D. R. P. 49970; E. P. 3333 of 1889). For example, aurintricarboxylic acid $C[C_6H_3(OH)CO_2H]_2 : C_6H_3(OH) : O$ can be obtained (*a*) by dissolving salicylic acid (2 parts) in concentrated sulphuric acid (15 parts) and methyl alcohol (4 parts), warming the solution to 60°–70° and adding solid sodium nitrite (1·5 parts) ; (*b*) by adding salicylic acid (2 parts) to a solution of sodium nitrite (1 part) in concentrated sulphuric acid (10 parts), and adding, with constant stirring, either formalin (0·5 part) or methylal (0·4 part) The product, a red powder, forms lakes with metallic oxides, of which that with chromic oxide is the most valuable, being fast to soap. The *ammonium* salt has found employment in calico-printing under the name chrome violet.

(2) **Methylaurin** $C_{20}H_{16}O_3$ crystallises in small brick-red crystals with a green metallic lustre. Bromine in acetic acid converts it into the compound $C_{20}H_{12}Br_4O_3$,HBr$+2H_2O$, which on boiling with water yields *tetrabromomethylaurin*; this dissolves in alcohol with a violet-red, and in alkalis with a magenta, colour. On reduction with zinc-dust and acetic acid, methylaurin yields the *leuco-* base $C_{20}H_{18}O$ crystallising in colourless rhombic needles (Z. *l.c.*; Monatsh. 3, 471).

(3) **Pseudorosolic acid** (*corallinphthalin* or *phenolcorallin*) $C_{20}H_{16}O_4$, is, together with other amorphous substances, the chief constituent of corallin. In colour it is red, with a green metallic lustre, and on oxidation with potassium permanganate yields corallinphthaleïn.

(4) Zulkowski (Monatsh. 16, 363) states that corallin, when prepared from pure phenol, contains, in addition to aurin, two colouring matters of the formulæ $C_{20}H_{16}O_4+H_2O$ and $C_{20}H_{16}O_5+H_2O$, of which the former is precipitated from solution in alkali by carbon dioxide, and the latter is not. Further, two isomeric substances, destitute of tinctorial properties,

of the formula $C_{19}H_{14}O_4$, are contained in the filtrate, after precipitation with carbon dioxide, and recovered from it by neutralisation with hydrochloric acid ; they are termed *α-* and *β-aurin oxides*. The nature of these four substances is unknown.

(5) In addition to the foregoing, **phenyl ortho-oxalate** $C_{14}H_{14}O_6$ sublimes during the preparation of aurin, and is found on the lids of the aurin pots in the form of colourless needles, melting at 128°. It plays no part, however, in the formation of aurin, but is produced by the action of phenol vapour on anhydrous oxalic acid (Claparède and Smith, Chem. Soc. Trans. 1883, 358 ; Staub and Smith, Ber. 17, 1740).

Pæonin (*red corallin* or *aurin R.*) is prepared by heating 2 parts of (yellow) corallin and 1 part of aqueous ammonia (sp.gr.=0·91) in an autoclave at 125°–140°, until a test shows the desired shade ; the product is then poured into water acidified with sulphuric acid.

Pæonin is a dark-red amorphous mass, with a green metallic lustre, and is a mixed product containing among other compounds some pararosaniline. It is insoluble in water, but soluble in alcohol and alkalis, yielding purple-red solutions ; acids do not affect the colour of its solutions. With wool and silk it gives shades intermediate between those of magenta and cochineal.

Closely related to aurin is **benzaurin** (*phenolbenzeïn*) $C_{19}H_{14}O_2$ or $\begin{matrix} C_6H_5 \\ OH \cdot C_6H_4 \end{matrix} \!\!>\!\! C : C_6H_4 : O$ obtained by gently heating 1 mol. of benzotrichloride with 2 mols. of anhydrous phenol, removing excess of phenol by steam distillation, extracting the residue with sodium bisulphite, and precipitating the filtrate with hydrochloric acid (Doebner, Ber. 12, 1462 ; compare Homolka, Ber. 18, 988). It crystallises in brick-red crystals, melts at about 100°, is insoluble in water, but soluble in alcohol, ether, and acetic acid. Alkalis dissolve it, yielding violet solutions. The *acetyl-* derivative melts at 119°. On reduction with zinc and hydrochloric acid, benzaurin is converted into dihydroxytriphenylmethane $C_{19}H_{16}O_2$.

Resorcinolbenzein $C_{38}H_{30}O_9$ (Doebner, Ber. 13, 610; Annalen, 217, 234; Aktieng. f. Anilinfab. in Berlin, D. R. P. 4322; E. P. 728 of 1878) is obtained by heating 1 mol. of benzotrichloride and 2 mols. of resorcinol at 180°–190°. It crystallises in large violet-red prisms, appearing yellow by transmitted light, is insoluble in water, ether, and benzene, has a yellowish-green fluorescence in dilute alcoholic solution, and yields a *bromo-* derivative which is sparingly soluble in all ordinary solvents, and dyes wool and silk in shades similar to those produced by eosin.

Rosolic acid (*rosaurin*) $C_{20}H_{16}O_3$ or $\begin{matrix} OH \cdot C_6H_4 \\ OH \cdot C_6H_3(CH_3) \end{matrix} \!\!>\!\! C : C_6H_4 : O$ is formed by diazotising rosaniline (Caro and Wanklyn, Chem. News, 14, 37 ; compare Zulkowsky, Monatsh. 16, 395).

Preparation.—500 grams of rosaniline are dissolved in 1½ litres of concentrated hydrochloric acid diluted with 1½ litres of water, and the filtered brownish-yellow solution diluted with 150 litres of water is treated with a dilute solution of sodium nitrite until the rosaniline has

almost but not quite disappeared. The whole is then heated gradually to boiling, and filtered after the evolution of nitrogen has ceased. On cooling, rosolic acid separates in lustrous brownish-green crystals, and is purified by dissolving in soda ley, saturating the solution with sulphur dioxide, filtering and precipitating the compound by addition of a mineral acid to the nearly colourless filtrate (Caro and Graebe, Annalen, 179, 192).

Properties.—Rosolic acid crystallises from dilute alcohol in ruby-red crystals, or in greenish scales with a metallic lustre, does not melt at 270°, and is insoluble in benzene and carbon bisulphide, very sparingly soluble in water, soluble in ether and acetic acid, and readily soluble in alcohol. In alkalis it dissolves with a red colour, which in very thin layers is bluish-red, and in thick layers is yellowish-red. In dilute solution the colour change from pale yellow to red on the addition of alkali is sufficiently sensitive to admit of the use of the acid as an indicator (Thomson, Chem. News, 47, 184). It is a feeble acid, and yields an unstable ammonium salt, crystallising in steel-blue needles. Bromine in acetic acid solution converts it into *tetrabromorosolic acid* $C_{20}H_{12}Br_4O_3$, which crystallises in lustrous green scales, dissolves in alkalis with a violet colour, and with reducing agents yields the *leuco-* compound. When heated with acetic anhydride at 150°–200°, it forms, among other compounds, triacetylleucorosolic acid (m.p. 148°–149°); *leucorosolic acid* $C_{20}H_{18}O_3$ itself being obtained by reducing rosolic acid either with sodium amalgam or with zinc-dust and soda ley (Caro and Graebe, *l.c.*).

A colour reaction for rosolic acid has been described by Alvarez (Ann. Chim. anal. 12, 9). To obtain it, 0·05–0·1 gram, with 0·2–0·3 gram of sodium peroxide, is mixed with 5 c.c. of alcohol, and after 4–6 minutes, 15 c.c. of water are added, when an intense purple colouration is obtained which is not destroyed by water.

Azulin or **Azurin.** Blue colouring matters to which these names have been given are obtained by heating (yellow) corallin with aniline (D. and S. Annalen, 166, 294; Guinon, Marnas and Bonnet, *l.c.*) or rosolic acid with aniline or various diamines. By substituting phenyl-hydrazine or other hydrazines for aniline, red dyes known as **rhodazines** are obtained (Ville, D. R. P. 98436; Eng. Pat. 16039, 27775 of 1896; D. R. P. 100555 of 1896), and analogous bluish-red dyes are formed when aurintricarboxylic acid (*v. supra*) or aurincarboxylic acid (Vidal, Eng. Pat. 5535, 5689, of 1897) are substituted for corallin or aurin.

The hexamethoxy- derivatives of aurin and rosolic acid are described under EUPITTONIC ACID (*q.v.*). W. P. W.

AURUM MUSIVUM or MOSAICUM. *Mosaic gold.* Made by triturating an amalgam of 2 parts tin and 1 of mercury with 1 part sal ammoniac and 1 of sulphur, and subsequently subliming. Used as a bronzing powder for plaster figures (*v.* BRONZE POWDERS).

AUSTENITE. A solid solution of carbon in iron, of variable composition; is a constant constituent of steels containing 1·1 p.c. of carbon or more when cooled rapidly from a temperature of 1100°–1500°. It may be obtained pure

by quenching a steel containing 0·93 p.c. carbon and 1·67 p.c. manganese from 1050° in ice-water (Maurer, Métallurgie, 1909, 6, 33). Steels containing 13 p.c. of manganese or 25 p.c. of nickel contain only austenite, and are soft and non-magnetic.

Under the microscope austenite is recognised by its softness as compared with [illegible] with which it is usually associated; by its structureless appearance and by the brightness of an etched, polished section (Le Chatelier, Revue de Métallurgie, 1904).

AUTAN. A mixture of solid (polymerised) formaldehyde and the dioxides of barium or strontium, used in the disinfection of living-rooms. On mixing the powder with water, a rapid disengagement of formaldehyde vapour, mixed with oxygen, occurs.

AUSTRALENE *v.* TURPENTINE.

AUSTRIAN CINNABAR. *Basic lead chromate (v.* CHROMIUM).

AUTOCLAVE. An apparatus constructed on the principle of Papin's digester, for heating liquids at temperatures above their boiling-points. Autoclaves are usually made of cast-iron or steel, occasionally of copper, and in some cases of sheet-iron or steel. Cast-iron autoclaves are sometimes strapped with steel rings for greater security. They are often enamelled or lined with sheet-tin, lead, copper, or zinc. Metallic linings are now soldered rigidly to the surface of the autoclave. They are fitted with a pressure gauge and safety valve, and tubes for the insertion of thermometers, and are usually closed by a screw or flanged cover, working against a leaden washer, and are heated either by the circulation of hot oil or in a bath of molten lead. As they have frequently to sustain pressures of from 20 to 30 atmos., they are tested before use by hydraulic pressure. Occasionally they are provided with agitators
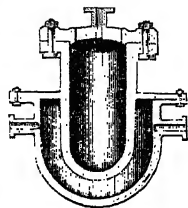
FIG. 1.
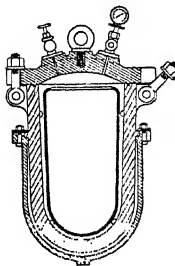
FIG. 2.
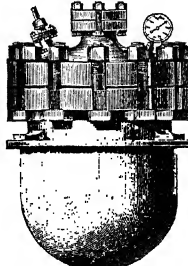
FIG. 3.

working through stuffing boxes, in order to ensure thorough mixing of the contents when heated.

Fig. 4 shows a method of withdrawing portions of the contents of an autoclave, or

adding liquid without removing the cover, when the apparatus is in use. The three-way valve A is adjusted so as to prevent passage through the pipe e. In order to withdraw a sample, the three-way cock B is made to communicate with b and d, and the valve A turned with a jerk so as to connect e with b ; the sample is then withdrawn at d. To completely remove the charge the valve A is left open for some time. In working without pressure the air-cock C is opened, and communication established between
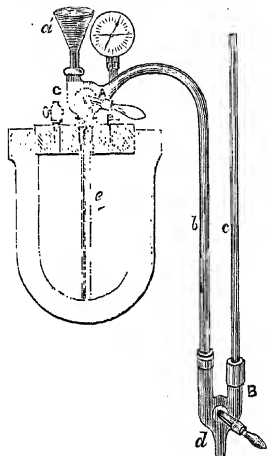
Fig. 4.

b and c and a' and b ; b and c are then filled with liquor identical in constitution with that contained in the apparatus obtained from a previous operation. The contents of the vessel are then removed by restoring the communication between e and b and b and d. To introduce liquor into the apparatus without removing the cover, the air-cock C is opened, and the funnel a' made to communicate with the pipe e by regulating the valve A.

Sometimes it is more convenient, as shown in Fig. 2, to provide a loose container for the substance under treatment.   J. W. H.

AUTOLYSIS. A physiological term signifying self-destruction, and used to indicate the destructive changes (apart from putrefaction due to micro-organisms) which occur in cells after death or removal from the living body. These changes are due to the action of intra-cellular enzymes, and are analogous to those which occur in digestion ; indeed the term auto-digestion is sometimes employed. The study of such changes is important because it is believed that the change after death, when the cells are still 'surviving' for a time, are identical with those which occur during life and result in the formation of waste substances, the products of vital activity. During life, however, the destructive changes are counterbalanced by changes in the opposite direction by which the cells build themselves up from food materials to repair their wear and tear. Assimilation of this kind is obviously impossible after death.

AUTUNITE or **CALCO - URANITE.** A mineral consisting of hydrated phosphate of uranium and calcium $Ca(UO_2)_2P_2O_8\cdot 8H_2O$, which within recent years has been somewhat extensively mined as an ore of uranium and radium. It is a member of the isomorphous group of minerals known as the 'uranium micas,' which crystallise in square, tetragonal (or very nearly square, orthorhombic) plates with a perfect micaceous and pearly cleavage parallel to their surface. In the orthorhombic autunite the colour is characteristically sulphur-yellow, or sometimes with a greenish tinge, so that this mineral is readily distinguished from the emerald-green torbernite or cupro-uranite. Spgr. 3·1 ; H. 2–2½. It occurs as an alteration product of pitchblende, and is often found as a scaly encrustation on the joint-planes of weathered granite or gneiss. The more important localities are St. Symphorien, near Autun in France (hence the name autunite) ; St. Just, Redruth, and Grampound Road in Cornwall ; Johanngeorgenstadt and Falkenstein in Saxony ; Black Hills in South Dakota ; and Sabugal, near Guarda in Portugal. At the last-named locality several mines have recently been opened up ; the crude ore is here leached with sulphuric acid, and the extracts sent to Paris for further treatment.   L. J. S.

AVA or *Kava-kava.* The root of *Piper methysticum* (Forst, f.), growing in the islands of the Pacific. It is taken as an intoxicant by the natives, and is used as a drug on the Continent. It is often adulterated with matico and annatto (Pharm. J. [3] 7, 149).

AVENTURINE or **AVANTURINE.** A variety of quartz found at Capa de Gata, Spain, spangled throughout with minute yellow scales of mica, is known as aventurine quartz. An aventurine felspar or sunstone is found at Tvedestrand, Norway. It is used for ornaments.

Artificial aventurine, or *glass,* or *gold flux,* was manufactured for a long period at the glassworks of Murano, near Venice. It may be prepared by adding to 100 parts of a not too refractory glass, 8 to 10 parts of a mixture of equal parts of ferrous and cuprous oxides, and allowing the mixture to cool very slowly so as to facilitate the formation of crystals.

Aventurine glaze for porcelain, invented by Wöhler (Annalen, 70, 57), is prepared by finely grinding 31 parts Halle kaolin, 43 quartz sand, 14 gypsum, and 12 porcelain fragments ; making the whole into a paste with 300 parts water, and adding successively 19 parts potassium dichromate, 47 lead acetate, 100 ferrous sulphate, and sufficient ammonia to precipitate the whole of the iron. After the soluble potash and ammonium salts have been washed out, the glazing is ready for use.

AVIGNON GRAINS. The seeds of *Rhamnus infectorius,* employed in dyeing for the production of yellow colours (*v. Rhamnin,* art. XANTHORHAMNIN).

AVOCADO PEAR or **ALLIGATOR PEAR.** The fruit of *Persea gratissima,* a tropical product. The fruit, which usually weighs from 4 to 6 oz., consists of rind (about 8 p.c.), flesh (67 p.c.), and a large 'stone' or 'pit' (about 25 p.c.). According to Prinsen-Geerlings (Chem. Zeit. 1897, 21, 715), the flesh contains :

Glucose	Fructose	Saccharose	Total sugar
0·40	0·46	0·86	1·72

The flesh, which has a nut-like flavour, is usually eaten with pepper and salt. An analysis, made by Jamieson (Chem. News, 1910, 102, 61), gave :

Water	Ether extract	Protein	Sugar	Fibre	Ash
66·9	10·6	5·7	1·1	4·0	2·0

The ether extract was green, and contained about 4 p.c. of resins. After their removal, an oil, resembling that of bergamot, was obtained, which had an iodine value of 29·9, and saponification value of 207.   H. I.

AVOCADO PEAR, OIL OF. An oil obtained from the oleaginous fruit of the *Persea gratissima*. Hofmann stated that for the purposes of the soapmaker this oil would be as valuable as palm oil.

AWAL or *Tarwar*. An Indian drug, the bark of *Cassia auriculata* (Linn.) (Dymock, Pharm. J. [3] 7, 977).

AWLA *v.* AMLAKI.

AXIN. A waxy secretion of a Mexican rhynchotrous insect *Llaveia axinus* which feeds on *Spondias lutea*, *Xanthoxylum Clava-herculis*, and *X. pentanome :* has the consistence of butter, the smell of rancid fat, and a yellow colour. Melts at 38°, and is soluble in hot alcohol and ether. Rapidly absorbs oxygen from the air, becoming brown, hard and insoluble in alcohol and ether. Is readily saponified, yielding *axinic acid* and glycerol. It resembles Japan lac and forms an excellent lacquer for wood, metals, and pottery (Bocquillon, J. Pharm. Chim. 1910, 2, 406; J. Soc. Chem. Ind. 29, 1320).

AZADIRACHTA, *Margosa*, or *Nim*. The bark of the nim tree. *Melia indica* (Brandis) [*M. Azadirachta*], is commonly used in India as a tonic and febrifuge. It contains a bitter resin. An oil, used in medicine and for burning is expressed from the seeds, which on saponification yielded 35 p.c. of fatty acid melting at 30°, and 65 p.c. melting at 44°.

AZELAIC ACID. *Lepargylic acid.* $CO_2H\cdot(CH_2)_7\cdot CO_2H$. It is obtained by oxidising Chinese wax (Buckton, J. 1857, 303), cocoanut oil (Wirz, Annalen, 104, 261), or castor oil (Arppe, Annalen, 124, 86) with nitric acid ; by the oxidation of oleic acid with potassium permanganate and caustic potash (Ehmed, Chem. Soc. Trans. 1898, 627), and by the oxidation of keratin (horn shavings) with permanganate (Lissizin, Zeitsch. physiol. Chem. 1909, 226). It is formed together with other products when fats or oleic acid become rancid (Scala, Chem. Zentr. 1898, i. 439). It has been synthesised from pentamethylene bromide and sodium acetoacetate (Haworth and Perkin, Chem. Soc. Trans. 1894, 86), and has been obtained by decomposing the ozonide of oleic acid (Molinari and Soncini, Ber. 1906, 2735 ; Harries and Thieme, *ibid.* 1906, 2844 ; Molinari and Fenaroli, *ibid.* 1908, 2789). It is best prepared by oxidising with potassium permanganate an alkaline solution of ricinoleic acid obtained by the hydrolysis of castor oil (Maquenne, Bull. Soc. chim. 1899, (iii.) 21, 106 ; Hazura and Grüssner, Monatsh. 9, 475). Azelaic acid crystallises in colourless plates, m.p. 106·2° (Massol, Bull. Soc. chim. [3] 19, 301), and is readily soluble in alcohol, less soluble in water or ether. By heating azelaic acid with soda lime, *azelaone (cyclononanone)* $C_8H_{14}O$, b.p. 205° (*circa*), is obtained

(Miller and Tschitschkin, Chem. Zentr. 1899, ii. 181); Harris and Tank (Ber. 1907, 4555) have shown that a complex mixture of cyclo-ketones is obtained by distilling the calcium salt of azelaic acid. *Azelaic anhydride* is obtained by heating azelaic acid with 7–8 pts. of acetyl chloride. It melts at 56°–57° (Étaix, Ann. Chim. Phys. [7] 9, 399).

AZELAONE *v.* AZELAIC ACID.

AZIDINE BLACK, -BLUE, -BORDEAUX, -BROWN, -FAST RED, -FAST SCARLET, -GREEN, -ORANGE, -PURPURINE, -YELLOW, -VIOLET, -WOOL BLUE *v.* AZO- COLOURING MATTERS.

AZIMINOBENZENE *v.* DIAZO COMPOUNDS.

AZIMINONAPHTHALENES *v.* DIAZO COMPOUNDS.

AZINES (Quinoxalines).   **Azonium bases, and colouring matters derived from them.**

Definition.—The term 'azines' has been given to a group of organic bases, which contain in their molecule as an intrinsic part of their constitution a heterocyclic hexagonal ring, built up of four carbon and two nitrogen atoms, arranged in such a manner that the nitrogen atoms stand in para-position to each other, whilst the four carbon atoms are disposed in two pairs between them, thus :

The term 'azine,' first proposed by Merz, is not happily chosen, and is even misleading, as it enters into the names of other nitrogen compounds of a different constitution, such as the hydrazines.

The name 'quinoxaline' was given by Hinsberg to compounds which also correspond with the above definition. It was, therefore, considered for some time as synonymous with the word 'azine,' which latter was, however, more frequently used. In later years it has become customary to distinguish between the two terms, and to use them for the two tautomeric forms in which these bases occur (*see Theory*).

The name 'azonium bases' has been given by Witt to a class of organic bases, derived from the azines by the linking of an organic radicle to one of the nitrogen atoms, whereby this atom passes from the trivalent into the pentavalent state, a process which results in a very marked change of the properties of the substance.

Both the azines and azonium bases possess the nature of powerful chromogens, the heterocyclic ring above mentioned being endowed with strong chromophoric properties. Being highly basic and capable of assuming a quinonoid structure (*see Theory*), they, and especially the azonium bases, possess to some extent the nature of dyestuffs, which is, however, much more strongly developed by the introduction of separate auxochromic groups. A very large number of powerful colouring matters of great intensity, variation, and purity of shade may thus be obtained, some of which have acquired considerable practical importance. According to their constitution, which is in almost all cases completely cleared up, they have been classified into groups, which have received the names

eurhodines, eurhodols, safranines, safranols, aposafranines, indulines, and fluorindines.

The investigation of the azines and their derivatives, which was accomplished by a number of chemists during the last 20 years of the nineteenth century, has been of considerable importance in the development of our present views on the constitution of colouring matters, and especially in the adoption of the modern quinonoid structural formulæ for the great majority of them.

History.—The two simplest and most typical members of the azine group, diphenazine and dinaphtazine, have been known for many years as ' azophenylene ' (Claus and Rasenack, 1873; Annalen, 168, 1) and 'naphtase' (Laurent, 1835; Ann. Chim. Phys. 59, 384), but their constitution was not properly understood and their importance not recognised. Merz (1886, Ber. 19, 725) finally proved the constitution of the former, which had been insufficiently substantiated by Claus, and proposed for it the name diphenazine; Witt (1886, Ber. 19, 2791) determined the true nature of 'naphtase.' In 1884 Hinsberg (Ber. 17, 319) described a general method for preparing his quinoxalines, which proved most fruitful in the further development of the subject. Other general methods were discovered by Witt, Merz, Japp, Ullmann, and others.

The first eurhodines were prepared by Witt in 1879 and 1885. He recognised that they formed a new class of dyestuffs, and also that they were related to the safranines. He determined their constitution in 1886 (Ber. 19, 441) by showing that they are the amino- derivatives of the azines or quinoxalines. At the same time he discovered the first eurhodol. The natural consequence of this discovery was the clearing up of the nature of the safranines, which were recognised in the same year simultaneously and independently by Witt, Nietzki, and Bernthsen as diamino- derivatives of the (then hypothetical) azonium bases. The first representative of this new class of bases was prepared in 1887 by Witt (Ber. 20, 1183).

The subject was now taken up and rapidly advanced by many chemists, amongst whom Nietzki and his collaborators, Kehrmann, Ullmann, and their collaborators, may be cited. Otto Fischer and Hepp also did a considerable amount of work in this domain, and especially in the investigation of the indulines and aposafranines.

The typical indulines and safranines have been discovered by purely empirical methods in the early days of the colour industry. The simplest representative of the group, *phenosafranine*, was prepared by Witt in 1877. Its phenylated derivative is *mauveïne*, the first artificial dyestuff prepared by W. H. Perkin in 1856.

Theory.—It has been already stated that the essential part of the molecule of an azine is the heterocyclic ring consisting of two atoms of nitrogen and four of carbon. Each of these six atoms has three atomicities engaged in the formation of the ring; the nitrogen atoms have, therefore, no free atomicities left (so long as they remain in the trivalent condition), whilst each of the carbon atoms has one atomicity free to be saturated by hydrogen or another monovalent

element or radicle. The simplest possible compound of the kind would thus have the formula $C_4N_2H_4$. It seems natural to suppose that it would be the prototype of all the azines.

Such a compound exists and is well known. It has received the name *pyrazine*. Many derivatives of it, formed by the substitution of its hydrogen atoms by monovalent organic radicles are also known; they form the large and well-investigated class of the ketine or aldine bases. But neither pyrazine itself (which in its properties resembles pyridine, to which it stands in the same relation as pyridine stands to benzene) nor the ketines show any resemblance to the typical azines. They exhibit no colourations, nor do they form any derivatives which have the nature of dyestuffs. For this reason pyrazine and the ketines are no longer considered as belonging to the azine group.

The characteristic properties of the azines only appear in compounds in which at least one other ring system is linked to the pyrazine ring, in such manner that one of the C_2-groups of the latter becomes part of an aromatic radicle. The process may be repeated. Thus the simplest representatives of the azine group would be compounds of the following type :—
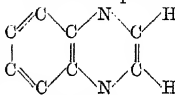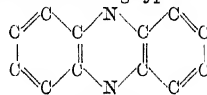
Phenazine. Diphenazine.

The nomenclature of the true azines has been chosen accordingly. The aromatic radicle or radicles linked to the central (or ' meso -') ring are prefixed to the syllables -azine.

The azines are members of the aromatic series. If we consider them as such, we recognise at once a strong analogy to other substances which contain heterocyclic rings linked to aromatic radicles, such as :
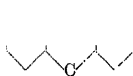
Anthraquinone. Acridine.
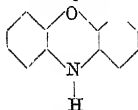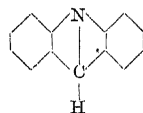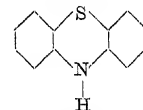
Oxazine. Thiazine.

all of which are chromogens, like the azines.

If we consider the manner in which the six atomicities of the two nitrogen atoms contained in the meso- ring of an azine may be disposed, we recognise two possibilities which are represented in the following structural formulæ of diphenazine :—
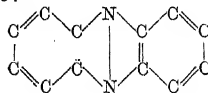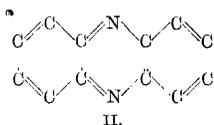
II.

Formula I. is the one first proposed by Claus for his 'azophenylene,' and by Merz for his azines; II., the one suggested by Hinsberg for his quinoxalines. Practically, there is no difference between azines and quinoxalines; they form one group; but it has been for a long time a matter of opinion which of the above formulæ was more adapted to the properties of these substances. Formula I. explains by its perfect symmetry the extreme stability of the azines, the fact that they may all be distilled without the slightest decomposition at extremely high temperatures. Formula II., on the other hand, is distinctly (ortho-) quinonoid, and consequently suggestive of chromogenic properties.

The existing difference of opinion as to the constitution of the azines has been finally disposed of by the admission that the azines are undoubtedly tautomeric, capable of assuming either of the constitutions I. and II., according to circumstances. In their free state, in which they are volatile and almost colourless, they possess the symmetrical (azine-) constitution I., whereas in their intensely coloured salts they have more probably the asymmetrical, quinonoid (quinoxaline-) constitution II. In the colouring matters derived from the azines, the case is frequently complicated by the fact that the auxochromic groups participate in the formation of the quinonoid constitution, which, by that means, may become *para-* as well as *ortho-*quinoid. Sometimes it is difficult to decide between the existing possibilities.

Synthetical methods for the production of azines, and their derivatives and description of some typical representatives of the group.

I. Azines. (a) *Synthetical methods.* (These will be referred to in the description of typical representatives by their number.)

1. By heating α-nitronaphthalene with powdered quicklime, Laurent (Ann. Chim. Phys. 59, 384) obtained dinaphthazine, which he called naphthase. Doer (Ber. 3, 291) and Klobukowski (Ber. 10, 573) modified the method by replacing the quicklime by zinc-dust. Schichuzky (J. R. 6, 2464) used lead oxide.

Wohl and Aue (Ber. 34, 2443) observed (1901) that nitrobenzene gives considerable quantities of diphenazine on being heated with strong caustic soda, a reaction which is practically identical with the one discovered by Laurent.

2. Claus and Rasenack (Annalen, 168, 1) obtained 'azophenylene' (diphenazine) by the dry distillation of orthoazobenzoic acid in the shape of its calcium or potassium salt. Claus proposed the azine formula for his product, but failed to afford convincing proofs for it.

3. A general method of great applicability was indicated by Hinsberg (Ber. 17, 319; 18, 1228), who showed that whenever an *alpha-* or *ortho-*diketone reacts on an aromatic orthodiamine, two molecules of water are given off and an azine is formed. The method was first applied to the production of phenazine:
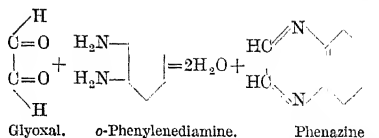
Glyoxal. o-Phenylenediamine. Phenazine (quinoxaline).

It works in most cases so well, that it has been recommended by its author (Annalen, 273, 343, 371) as the best method of identifying either an orthodiamine or an orthodiketone. Very small quantities of the ingredients are necessary, and the azine formed is easily recognised by its melting-point and sulphuric acid reaction.

Hinsberg's reaction may be extended to nitroso-β-naphthol, which is in reality the oxime of ortho-naphthaquinone. Ullmann and Heisler obtained (Ber. 42, 4263) naphthaphenazine by heating ortho-phenylenediamine hydrochloride with nitroso-β-naphthol:
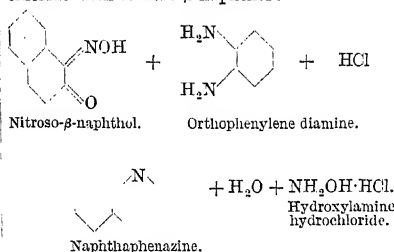
Nitroso-β-naphthol. Orthophenylene diamine.

Naphthaphenazine.

$+ H_2O + NH_2OH \cdot HCl.$
Hydroxylamine hydrochloride.

4. The method of Merz (Ber. 19, 725) is of less general application. It consists in the action of orthodihydroxyl- derivatives upon orthodiamines: the hydro- derivatives of the azines are formed, and these are oxidised by the oxygen of the air into the azines:
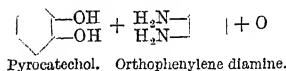
Pyrocatechol. Orthophenylene diamine.
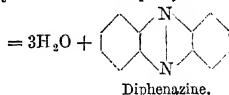
Diphenazine.

5. Early investigators had studied the reaction of ammonia under pressure upon benzoin (Erdmann, Annalen, 135, 181) and phenanthraquinone (Sommaruga, Monatsh. 1, 146). Japp and Burton showed that the free ammonia may be advantageously replaced by ammonium acetate, and proved that the 'ditolane azotide' and 'phenanthrene azotide' obtained were tetraphenylketine and diphenanthrazine. They generalised the method and applied it to β-naphthaquinone, from which they obtained dinaphthazine (Chem. Soc. Trans. 1887, 98).

6. Another mode of formation of the azines consists in the joint oxidation of a phenol, in which the *para-* position is no longer open to substitution, and aromatic orthodiamines. This method was discovered by Witt (Ber. 19, 917), who used it for the production of a new isomeride of tolunaphthazine by oxidising a mixture of β-naphthol and orthotolylene diamine:

β-Naphthol.   Orthotolylene diamine.

Tolunaphthazine.

7. An elegant modification of the above method was devised in 1905 by Ullmann and Ankersmit (Ber. 38, 1811), who heated β-naphthol with orthoaminoazotoluene. The latter takes up the hydrogen liberated in the reaction, yielding at the same time the necessary orthodiamine.

β-Naphthol.   Orthoaminoazotoluene.

Tolunaphthazine.

8. A very peculiar mode of formation of these substances was discovered by Witt (Ber. 20, 571), who showed that the orthoazo- derivatives of secondary amines, and more especially of such amines containing the β-naphthyl- group, are decomposed by being heated with acids into the corresponding azine and amino- compound, thus :

Benzene-azo-phenyl-   Naphthaphenazine.
β-naphthylamine.

The reaction is simple and easy, and gives, as a rule, excellent yields. It is in reality a condensation of the secondary amine into the corresponding azine by the dehydrogenating influence of the azo- group temporarily introduced for the purpose.

(b) *Generic characters of the azine group.* All azines have certain peculiar properties in com-

mon. As a rule, they are solid, well-crystallised compounds of white, pale yellow, or even orange colour, possessing a high melting-point, and boiling under atmospheric pressure at very high temperatures (in some cases approaching red heat) practically without decomposition. They sublime at temperatures below their boiling-point, and their vapours condense into voluminous aggregates of crystals.

All the azines are bases which form salts with acids. The mono-acid salts, with the stronger mineral acids, may generally be obtained in a crystallised condition ; but they are stable only in the presence of an excess of acid or in the absence of water, which easily decomposes them into their constituents. These salts are intensely coloured, a fact which justifies the inference that they contain the base in the quinonoid (quinoxaline) form. The hydrolytic action of the water is therefore accompanied by the tautomeric change into the symmetrical (azine) form. These salts, some of which have been analysed, invariably contain one equivalent of acid for one molecule of the base. The di-acid salts cannot be isolated, but evidence of their existence is given by the intense red, violet, or blue colourations exhibited by the solutions of azines in a great excess of strong acid, preferably sulphuric acid. If water be added to these solutions, a change takes place ; the di-acid salt is decomposed, the yellow or orange mono-acid salt is formed, and, on further addition of a large excess of water, the free azine itself separates out in flakes. These striking colour reactions are highly characteristic, and form the best means of identifying the azines.

Notwithstanding these intense colourations, the azines are not applicable as dyestuffs. They are only to be considered as chromogens and suitable to produce colouring matters by the introduction of auxochromic groups into their molecules. They are thus strictly analogous to the other heterocyclic chromogens such as anthraquinone, acridine, oxazine, and thiazine.

There is, however, one group of azines to which all the rules and general characteristics given above cannot very well be applied. These are the ' Indanthrenes,' certain azines of the anthracene group, which, owing to their large molecule and very complicated constitution, possess properties quite different from all the other azines. They are intensely coloured and extremely valuable as dyestuffs if applied to the textile fibre by the ' vat process ' like indigo. This peculiar mode of application brings them into close relationship with indigo, and they will therefore be treated in this work under INDIGO AND INDIGOID DYESTUFFS (*q.v.*).

(c) *Description of some typical representatives of the azine group.*

Diphenazine

$$C_{12}H_8N_2 = $$

(Claus, Annalen, 168, 1 ; Bernthsen, Ber. 19, 3256 ; Ris, Ber. 19, 2206 ; Wohl, Ber. 34, 2443) has been obtained by the methods 1, 2, and 4. It forms pale-yellow needles, of the m.p. 170°–171°, soluble in alcohol and most other solvents. It distils without decomposition. It dissolves

in strong acids, forming unstable salts of yellow and red colour.

Toluphenazine

$C_{13}H_{10}N_2$

has been prepared by Merz (Ber. 19, 725) by the action of pyrocatechol on orthotolylenediamine (method 4). It is very similar to diphenazine. Its m.p. is 117°, its b.p. 350°.

Naphthaphenazine

$C_{16}H_{10}N_2 =$

has been prepared by Witt (Ber. 20, 571). The best mode of obtaining it is by the decomposition, by acid, of the azo- compounds derived from phenyl-β-naphthylamine, but it has also been prepared by the action of β-naphthaquinone on orthophenylenediamine and by simultaneous oxidation of the latter and β-naphthol. It forms yellow needles, melting at 142·5°, distilling at a high temperature without decomposition, and dissolving in sulphuric acid with a reddish-brown colouration. On dilution, two sulphates crystallise from this solution. It is supposed that the formation of two series of monacid salts of this base is due to either of the two nitrogen atoms becoming pentavalent and saturated with the acid.

Tolunaphthazines $C_{17}H_{12}N_2$. Three substances of this formula are known, the isomerism of which has been discussed by Witt (Ber. 20, 577). One of these, melting at 179·8° has been prepared by the simultaneous oxidation (Ber. 19, 917) of orthotolylenediamine and β-naphthol (methods 6 and 7). Its constitution is expressed by the formula
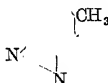
It dissolves in sulphuric acid with a violet colouration. The other is formed by the decomposition by acids of the azo- derivatives of paratolyl-β-naphthylamine (Ber. 20, 577) (method 8). Its constitution is represented by the formula
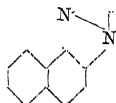
Its melting-point is 169°; its sulphuric acid reaction is similar to that of naphthaphenazine.

The third tolunaphthazine, discovered by Hinsberg (Annalen, 237, 343a, 371) (method 3), has been proved to consist of a molecular combination of the two preceding ones ; its melting-point is 139°–142°.

Several other tolunaphthazines are theoretically possible. They have not, however, hitherto been prepared.

Dinaphthazines $C_{20}H_{12}N_2$. It has already been stated that Laurent's mysterious 'naphthase,' prepared by method 1, finally proved to be dinaphthazine. It is probable that Laurent's product was a molecular combination of two of the four isomeric dinaphthazines foreseen by theory. A similar mixture may be obtained by reacting with αβ-naphthylenediamine upon β-naphthaquinone (method 2). This method was used by Witt in his identification of Laurent's 'naphthase' (Ber. 19, 2791). For preparing the constituents of this mixture in a pure state the synthetical method 8 should be resorted to ; it consists in the decomposition of the azo- derivatives of the two isomeric (α, β, and ββ)-dinaphthylamines (Matthes, Ber. 23, 1329 and 1333). The compounds thus obtained have the following constitutions and melting-points :—
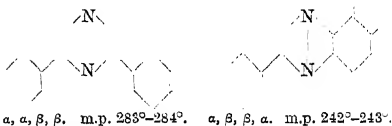
α, α, β, β. m.p. 283°–284°.   α, β, β, α. m.p. 242°–243°.

The two other possible isomerides :
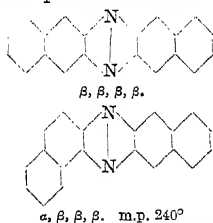
β, β, β, β.
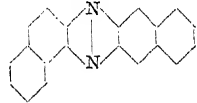
α, β, β, β. m.p. 240°

may be obtained from ββ-naphthylenediamine by the reaction of the two orthonaphthaquinones (method 2), but, so far, only the asymmetrical one has been prepared by Otto Fischer and Albert (Ber. 29, 2087).

Azines of the Phenanthrene group. Owing to the extreme facility and precision with which phenanthraquinone acts upon all orthodiamines, these azines are most easily prepared, and phenanthraquinone is commonly used for deciding the question whether any given aromatic diamine is an ortho- compound. A large number of azines has thus become known, of which only a few may be described as typical representatives of the group.

Phenanthraphenazine $C_{20}H_{12}N_2$ (isomeric with dinaphthazine) may be obtained by acting on orthophenylenediamine with either phenanthraquinone in an acetic acid solution (Hinsberg, Annalen, 237, 340), or with phenanthraquinone sodium bisulphite in an aqueous solution (method 2). It crystallises in pale-yellow

needles, melting at 217°, and dissolves in sulphuric acid with a beautiful red colouration. Its constitution is
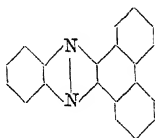
A similar substance may be obtained from orthotolylenediamine. It melts at 212°–213°.

Phenanthranaphthazine $C_{24}H_{14}N_2$ is easily obtained (Lawson, Ber. 18, 2426) from orthonaphthylenediamine and phenanthraquinone (method 2). It gives a violet colouration with sulphuric acid. M.p. 273°. The sulphonic acid derivatives of this substance, $C_{24}H_{13}N_2 \cdot SO_3H$, are obtained (Witt, Ber. 19, 1719; 21, 3485 *seq.*) by acting with an aqueous solution of phenanthraquinone sodium bisulphite upon the solutions of the various naphthylenediamine sulphonic acids in sodium acetate solution, acidulated with acetic acid. These sodium salts are soluble in pure water; very small quantities of alkaline salts are sufficient to precipitate them from these solutions.

Chrysotoluazine $C_{25}H_{16}N_2$ and **Chrysonaphthazine** $C_{28}H_{16}N_2$ have been prepared by Liebermann and Witt (Ber. 20, 2442) from chrysoquinone and the corresponding orthodiamines (method 2). The same authors obtained azine derivatives from the quinone of picene.

Tolustilbazine $C_{21}H_{16}N_2$ was discovered by Hinsberg, who described it under the somewhat misleading name ' Diphenyltoluquinoxaline ' (Annalen, 237, 339). It is typical of the many azines which may be obtained by the action of benzil upon aromatic orthodiamines.

It separates in silvery leaflets from an alcoholic solution of benzil mixed with a solution of orthotolylenediamine (method 2). It melts at 111°, and dissolves with a crimson shade in sulphuric acid. Its constitution is expressed by the formula
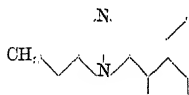
The corresponding derivative of orthonaphthylenediamine was prepared by Lawson (Ber. 18, 2426).

Toluindazine $C_{15}H_{11}N_3$, the azine derivative of isatine, has been prepared by Hinsberg (Annalen, 237, 344) from orthotolylenediamine and isatin, by melting together the ingredients (method 2) and crystallising the product obtained from a mixture of alcohol and acetic acid. It forms yellow needles, melting at 290°, and dissolving in acids with a brownish-red colouration. Its constitution is expressed by the formula
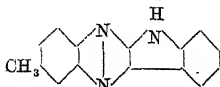
A large number of other less important azines have been prepared in experiments made with a view to showing that certain compounds obtained by the authors were either orthodiketones or orthodiamines.

II. Colouring matters derived from azines (eurhodines and eurhodols).

It has already been said that by the introduction of an auxochromic group, NH_2 or OH, into the molecule of an azine, the latter is transformed into a colouring matter. The aminoderivatives of azines containing either one or several amino- groups, are embraced by the generic name of *eurhodines*, whilst the name of *eurhodols* has been given to the phenolic (OH) derivatives of the azines. The following is an enumeration of the various methods by which eurhodines and eurhodols have been obtained :—

A. EURHODINES.

1. By heating together any orthamino-azocompound and the hydrochloride of certain aromatic monoamines, such as, for instance, α-naphthylamine or α-aminoquinoline, preferably in a phenol solution, monoamino-azines (the eurhodines proper) are obtained. It was by this process that the first eurhodine was discovered by Witt in 1883 (Ber. 18, 1119 ; 19, 441) by heating orthaminoazotoluene with naphthylamine hydrochloride. In this reaction an orthodiamine is formed by the reduction of the aminoazo compound, which combines with α-naphthylamine, hydrogen being eliminated and absorbed by the amino-azo- compound still present.

$$C_7H_{10}N_2 + C_{10}H_9N = 6H + C_{17}H_{13}N_3.$$
Orthotolylene- α-Naphthyl-   Typical
diamine.   amine.   eurhodine.
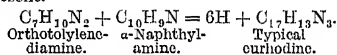
2. Another method of much greater applicability consists in reacting with α-diketones upon aromatic triamines, which contain two aminogroups in the ortho- position. Two molecules of water are eliminated for every molecule of eurhodine formed. Thus, for instance, a eurhodine was obtained from triaminobenzene and phenanthraquinone (Witt, Ber. 19, 445) :
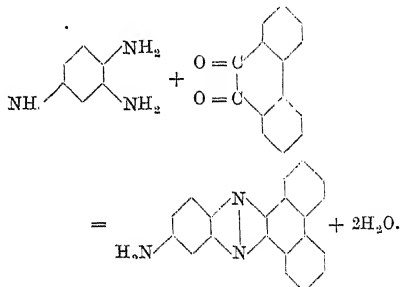
3. Another method of considerable applicability consists in heating together nitroso-amines (Witt, Ber. 21, 719) or quinonedichlorimides (Nietzki a. Otto, Ber. 21, 1598) with aromatic amines in which the para- position to the aminogroup is occupied by some radicle. Thus, for instance, a eurhodine is formed by heating together nitrosodimethylaniline hydrochloride and β-naphthylamine, in an acetic acid solution :
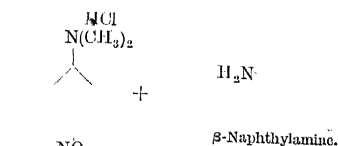
Nitrosodimethylaniline
hydrochloride.
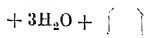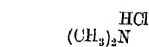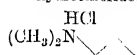
β-Naphthylamine.

Dimethylaminonaphthaphen-
azine hydrochloride.

Paraphenylenedime-
thyldiamine mono-
hydrochloride.

and an analogous, though somewhat different reaction takes place if the nitrosodimethylaniline be substituted by dichloroquinonimide.

Dichloroquinonimide.

Aminonaphthaphenazine.

4. Eurhodines proper may also be obtained by the reduction (with ammonium sulphide) of nitro-azines. Thus, for instance, nitrophenophenanthrazine may be reduced into the eurhodine aminophenophenanthrazine (Heim, Ber. 21, 2306).

5. If certain azo- colours, such as chrysoïdine, be heated with β-naphthol, an eurhodine is formed: (Ullmann and Ankersmit, Ber. 38, 1812):

Chrysoïdine.

β-Naphthol.
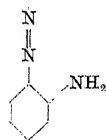
Eurhodine.
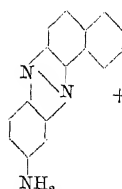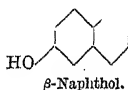
$+C_6H_5NH_2+H_2O$
Aniline.
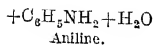
6. Diaminoazines are formed by the decomposition of certain indamines when their solutions are boiled for a certain time. Thus tolylene blue, the indamine produced by the action of nitrosodimethylaniline hydrochloride upon metatolylenediamine, is decomposed if its solution be boiled for some time, dimethyldiaminotoluphenazine (tolylene red) being the principal product of this reaction (Witt, Ber. 12, 931):

Tolylene blue.   Leucotolylene blue.   Tolylene red (dimethyldiaminotoluphenazine).

7. Di- and polyamino- azines may also be prepared by the oxidation of orthodiamines and of polyamines containing two amino- groups in the ortho- position. Thus O. Fischer and E. Hepp proved (Ber. 22, 355) that the red substance which is formed by the oxidation of orthophenylenediamine and which has been observed by many investigators (Griess, Ber. 5, 202; Salkowski, Annalen, 173, 58; Rudolph, Ber. 12, 2211; Wiesinger, Annalen, 224, 353), is nothing else than diaminophenazine. And Nietzki and Müller obtained (Ber. 22, 447) by oxidising tetra-aminobenzene with a current of air tetra-aminophenazine. Aminooxyphenazines may sometimes be found as by-products in this reaction (Ullmann and Mauthner, Ber. 35, 4302 and *ibid.* 36, 4026).

B. Eurhodols.

These may likewise be prepared by various methods.

1. The sulphonic acids of azines, fused with potash, readily yield the corresponding oxyazines or eurhodols (Witt, Ber. 19, 2791). For instance:
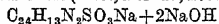
$C_{24}H_{13}N_2SO_3Na+2NaOH$
Sodium naphthaphenanthrazinesulphonate.
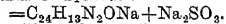
$=C_{24}H_{13}N_2ONa+Na_2SO_3$.
Phenanthranaphthaeurhodol.

2. Several eurhodines (amino-azines) yield the corresponding eurhodol on being heated under pressure with strong acids, a hydrolysis taking place in the circumstances (Witt, Ber. 19, 444):
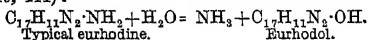
$C_{17}H_{11}N_2 \cdot NH_2+H_2O = NH_3+C_{17}H_{11}N_2 \cdot OH$.
Typical eurhodine.   Eurhodol.

3. Diazo-azines, on being boiled with water, yield the corresponding eurhodols ; on being boiled with alcohol they yield the alkyl ethers of these eurhodols (Witt, Ber. 19, 444) :

$C_{17}H_{11}N_2 \cdot N : N \cdot Cl + H_2O$
Diazoeurhodine chloride.

$= HCl + N_2 + C_{17}H_{11}N_3OH.$
Eurhodol.

$C_{17}H_{11}N_2 \cdot N : N \cdot Cl + C_2H_5OH$
$= HCl + N_2 + C_{17}H_{11}N_2OC_2H_5.$
Ethyleurhodol.
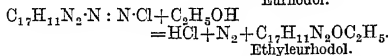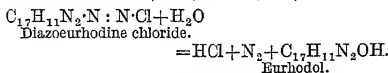
The following is an enumeration of those of the eurhodines and eurhodols which have been more closely investigated, the properties of which are typical for the whole class of colouring matters :—

Typical eurhodine $C_{17}H_{13}N_3$ (Witt, Ber. 19, 445). The mode of formation of this substance has already been given (Section A, 1). It is best prepared by heating to 130° equal molecules of orthoaminoazotoluene, of the melting-point 118·5°, and α-naphthylamine hydrochloride, dissolved in phenol until the colour of the mixture, which is at first of an emerald green, has changed into a brilliant scarlet. The mixture is now treated with a large quantity of toluene, when the hydrochloride of the new dyestuff is precipitated in a crystalline state. By recrystallisation from water acidified with hydrochloric acid, it may be obtained in a pure state. From the pure hydrochloride the free eurhodine base is precipitated by alkalis or ammonia in the form of a yellow powder, which may be recrystallised from aniline. Thus prepared, it forms glistening yellow prisms and needles of a dark-brown colour. It dissolves in ether with a yellow colour and a magnificent green fluorescence, which is characteristic of all the members of this group of dyestuffs. Eurhodine forms three series of salts, of which, however, only those with one molecule of acid are fairly stable, whilst those containing more acid are decomposed by the addition of water. It is to the formation of these various salts that the peculiar change of colour is due which is observed on adding water to a solution of eurhodine in concentrated sulphuric acid. This solution is of a cherry-red colour. On adding a small quantity of water the colour changes to a fine emerald green, whilst still more water produces the scarlet shade of the normal sulphate. This change of colour, which is observed with all the eurhodines, links them to their parent-substances, the azines, which exhibit similar curious phenomena, and also to the safranines.

The normal salts of eurhodine are well crystallised and of a bronzed copper colour when solid. In solution they exhibit a bright scarlet tint which they communicate to the fibre. These normal salts are, however, partially decomposed by an excess of water, the free eurhodine base being regenerated. The same takes place if fibres dyed red with eurhodine be washed. The scarlet shade is gradually replaced by the yellow shade of the free eurhodine base. For this reason eurhodine has not found an application in the industry of artificial dyestuffs.

Aminonaphthaphenazine $C_{18}H_{11}N_3$ has been obtained by Nietzki and Otto (Ber. 21, 1598) from β-naphthylamine and dichloroquinonimide (Ullmann and Ankersmit, Ber. 38, 1811). It crystallises in dark-yellow needles. Its salts are

of a crimson colour. Its solution in sulphuric acid changes by the addition of water from reddish-brown through green into red. It forms a diazo- compound which, when boiled with alcohol, yields the ordinary naphthaphenazine, of the melting-point 142·5°. The following compound is its dimethyl derivative :—

Dimethylaminonaphthaphenazine $C_{18}H_{15}N_3$ (Witt, Ber. 21, 719). This eurhodine, the formation of which has been described under Section A, 3, may easily be prepared in quantity by heating together 20 parts nitrosodimethylaniline hydrochloride and 10 parts β-naphthylamine with 50 glacial acetic acid ; the reaction sets in below 100°, and is apt to become violent. The product changes to a fine violet colour. It is dissolved in water acidified with hydrochloric acid, and the filtered solution is precipitated by the addition of sodium acetate. The crude eurhodine which is thus precipitated may be purified by dissolving it in alcohol acidified with hydrochloric acid. From this solution the normal eurhodine hydrochloride crystallises in bronze-coloured needles. From these ammonia liberates the free eurhodine base in the form of a scarlet crystalline powder. It may be recrystallised from boiling xylene ; it is thus obtained in magnificent crystals resembling magnesium-platinocyanide, melting at 205°.

The change of colour of a sulphuric acid solution of this eurhodine is not very marked, going from violet through black and green into violet. The ethereal solution of the free base exhibits the brilliant fluorescence characteristic of all eurhodines.

Aminophenaphenanthrazine $C_{20}H_{13}N_3$. This eurhodine was prepared by Witt (Ber. 19. 445) and by Heim (Ber. 21, 2306) by the methods given under Section A, 2 and 4. It crystallises from toluene in short, thick, yellow prisms, melting at 279°.

Dimethyldiaminotoluphenazine ; Tolylene red $C_{15}H_{16}N_4$. The formation of this compound by the spontaneous decomposition of tolylene blue has been described under Section A, 5. This eurhodine forms, in a pure state, orange crystals, which contain 4 mols. of water of crystallisation ; at 150° this is given off and the anhydrous base remains as a dark-red powder. The hydrated base is soluble in ether with a pink colour and a beautiful orange fluorescence. The solution in concentrated sulphuric acid is green ; on being diluted with water it changes through sky-blue into red. The normal (monacid) salts are perfectly stable and soluble in water with a pink colour. This solution dyes unmordanted or mordanted cotton and other fibres a pink which in darker shades deepens into a coppery red.

The production of this dyestuff has been patented (Otto N. Witt, D. R. P. 15272). The commercial product, which contains a certain amount of impurities, is sold under the name of 'neutral red.' It is chiefly used in calico-printing, and gives very fast and useful shades.

A similar product is prepared from the indamine which is formed by reacting with nitrosodimethylamine hydrochloride upon metaphenylenediamine. It is embraced by the same patent and sold under the name of 'neutral violet.'

Typical eurhodol $C_{17}H_{11}N_2OH$ (Witt, Ber.

19, 444). This substance, the formation of which takes place according to the equation given under Section B, 2, forms small leaflets of a yellow or red colour which dissolve in concentrated sulphuric acid with a red colouration, and are reprecipitated from this solution by the addition of water. Caustic soda solution dissolves it with an orange shade. Thus it is shown that this eurhodol (like all compounds of the same class) exhibits both acid and basic properties, the latter being due to the azine group contained in their molecule.

Eurhodol $C_{24}H_{14}N_3OH$. α-Hydroxynaphthaphenanthrazine has been obtained (Witt, Ber. 19, 2791) by the method described under Section B, 1, by the fusion of naphthaphenanthrazine-α-sulphonic acid with caustic alkalis. Its solution in sulphuric acid is of a fine and intense indigo-blue; it changes very suddenly into red on the addition of water, the sulphate being precipitated. This substance is a yellow colouring matter which may be fixed on cotton with alum-mordant, like alizarin. Owing, however, to its costliness, it has not been brought into commerce. A large number of isomerides may be prepared by starting from the numerous sulpho- derivatives of orthonaphthylenediamine, transforming them into azinesulphonates by condensation with phenanthraquinone and into eurhodols by subsequent fusion with caustic alkalis.

III. **Azonium bases and safranines.** The azonium bases are a class of compounds of which our knowledge is very restricted, very few representatives of the class being at present known, and that rather imperfectly. They are, however, of importance, as it is now established beyond doubt that they are the parent substances of the very important class of dyestuffs known as safranines. Although the first artificial dyestuff, mauveïne, was a true safranine, and although this group of compounds has been frequently under investigation, a correct view of their constitution had not been obtained until quite recently. According to the theory now universally adopted, all safranines are amino- derivatives of azonium bases, to which they stand in the same relation as the eurhodines to the azines. Hydroxy- derivatives of azonium bases have also been prepared and described under the name of safranols. They are, however, of no importance as colouring matters.

The azonium bases themselves, none of which has so far been obtained in a state fit for analysis, stand in the same relation to the azines as the ammonium bases to the amines. They are azines in which one of the nitrogen atoms has become pentavalent by being saturated with three organic radicles and one acid radicle, the connection with the second nitrogen atom being still preserved by the fifth valency of the pentavalent nitrogen atom. Thus the characteristic constitution of the azonium compounds may be expressed by the general formula

$$R^{II} \diagdown \begin{matrix} N^{III} \\ | \\ N^V \end{matrix} \diagup R^{II}$$
$$R^I \quad X^I$$
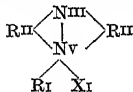
in which R^I and R^{II} represent mono- and

divalent organic radicles, and X^I a monovalent acid radicle. The azonium bases are compounds which possess strong basic properties, and which, by the tenacity with which they retain their acid radicle, strongly resemble the ammonium bases. It is probable that the free azonium bases contain, like the ammonium bases, the hydroxyl group in the position X^I of the above general formula. The azonium bases and the dyestuffs derived from them are also capable of tautomeric changes, which lead to their assuming quinonoid structures. The nature of these changes are in many cases doubtful and too complicated to be fully discussed in this article.

The azonium bases are strongly coloured substances, but their dyeing properties are developed and brought to perfection by the introduction of amino- groups into their molecule. As the azonium bases theoretically possible are very numerous, and each of them is capable of producing very numerous isomeric mono- and polyamino- derivatives, the number of possible safranines is exceedingly large, and the number of those which have already been prepared is insignificant in comparison with that foreshadowed by theory.

Of the safranines which have hitherto been prepared, only a few are monoamino- derivatives of azonium bases. A few more are of doubtful or unknown constitution. The majority are asymmetric diamino- derivatives of azonium bases, containing one amino- group in one of the diatomic organic radicles (R^{II}, whilst the other is attached to the monoatomic radicle (R^I).

The true constitution of phenosafranine and its congeners has been recognised by Witt, who, after pointing out the analogy between the eurhodines and safranines (Ber. 18, 1119) and clearing up the constitution of the former (Ber. 19, 446), proved the latter to be asymmetric diaminoazonium bases (Ber. 19, 3121). Bernthsen had proposed (Ber. 19, 2690) somewhat earlier a symmetrical formula for the safranines based upon Witt's eurhodine researches. His view was subsequently adopted by some chemists, but the author of this article fails to see the force of the arguments adduced in support of it.

A. **Azonium bases.** 1. The typical compound was obtained by Witt (Ber. 20, 1183) by the reaction of phenanthraquinone on phenylortho·naphthylenediamine. By heating these ingredients in an acetic acid solution an intermediate product is obtained, which on treatment with a mineral acid is transformed into the salt of the azonium base :
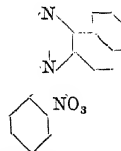
If nitric acid is used, the nitrate is deposited in very fine crystals. It is sparingly soluble in water, readily soluble in spirit with a fine orange-red colouration. The hydrochloride dissolves in sulphuric acid with a violet tint, which changes into red on dilution with water.

2. If in this reaction the phenylorthonaphthylenediamine be replaced by phenylorthophenylenediamine, the resulting compound is a yellow dyestuff of considerable strength. It is manufactured and sold under the name 'Flavinduline' (1893).

3. A very similar compound was obtained by Otto N. Witt and Christoph Schmidt in 1892 (Ber. 25, 1017), by the reaction of benzil upon ethoxyphenylorthonaphthylenediamine. It was called ethoxyphenylnaphthostilbazonium chloride and has the constitution:
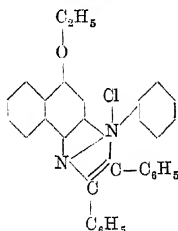
It is a beautiful yellow dyestuff, but too expensive to be prepared on a manufacturing scale.

B. Safranines. The various colouring matters belonging to this group have mostly been prepared by different synthetical methods, which may be classed in the following manner :—

1. Reduction of the nitro- derivatives of azonium bases. By reacting with mononitrophenanthraquinone or dinitrophenanthraquinone on phenylorthonaphthylenediamine, nitro- and dinitro- derivatives of the above azonium base are obtained, which on reduction with ammonium sulphide yield reddish-violet colouring matters belonging to the safranine group (Witt, unpublished observations).

2. If the stilbazonium base obtained by Witt and Schmidt, or any of its congeners prepared from ethylated arylorthonaphthylenediamines be heated with ammonia, the ethoxy group is replaced by the amino- group and the corresponding safranines are formed. This is quite a general reaction (Witt and Schmidt, Ber. 25, 2003 ; Witt and v. Helmolt, Ber. 27, 2355 ; Witt and Buntrock, Ber. 27, 2362).

3. By the action of dichloroquinonimides upon secondary aromatic amines, in which the para- position to the amino- group is occupied, monoamino-azonium bases are formed (Nietzki and Otto, Ber. 21, 1598). The reaction, for instance, between dichloroquinonimide and phenyl-β-naphthylamine may be represented by the equation :

Dichloroquinonimide.   Phenyl-β-naphthylamine.
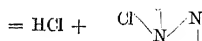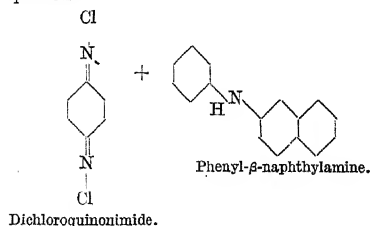
New dyestuff.

4. In a similar manner nitrosodimethylaniline (or any other nitroso-amino) reacts with phenyl-β-naphthylamine (Witt, Ber. 21, 719):

Nitrosodimethylaniline hydrochloride.   Phenyl-β-naphthylamine.

New dyestuff.   Dimethylparaphenylenediamine monohydrochloride.
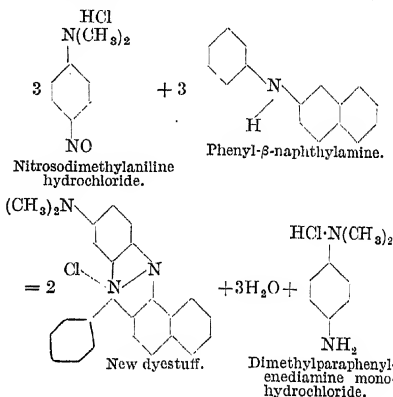
5. The safranines proper (asymmetric diaminoazonium bases) are formed by the joint oxidation of one molecule of diamine and two molecules of an aromatic monoamine. In this reaction fugitive indamines are formed as intermediate products ; the process thus becomes strictly analogous to the formation of toluylene red and its congeners.

This is the process which is generally used in the manufacture of safranines, and it will therefore be fully explained.

By the joint oxidation of an aromatic paradiamine with one molecule of an aromatic monoamine, an indamine is invariably formed (v. INDAMINES). If these indamines be oxidised in the presence of another molecule of an aromatic monoamine, a safranine is formed :

First Stage.

Paraphenylenediamine.   Aniline.   Indamine.

. Second Stage.

NH_2 + $+2O = 2H_2O +$ (HCl NH_4)   N⟩N Cl

Aniline hydrochloride.

NH
Indamine.

Phenosafranine.

NH_2 + NH_2HCl . $+3O = 3H_2O +$

Aniline hydrochloride.

NH_2
Dipara-amino-diphenylamine.
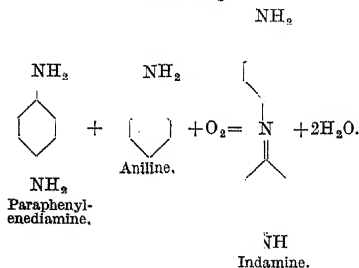
Safranine.
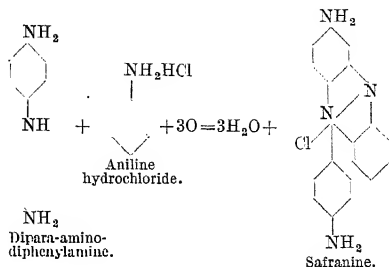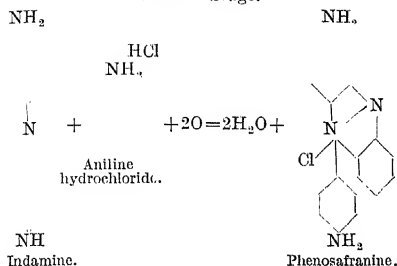
Of course, any other paradiamine may be substituted for paraphenylenediamine, and any other monoamine for aniline. As, however, the formation of an indamine only takes place if the para- position to the amino- group be still free, it results, that at least one of the two molecules of monoamines must fulfil this condition. Thus the formation of a safranine from paraphenylenediamine takes place on oxidation of one molecule of the diamine with

(1) Two molecules of aniline.
(2) Two molecules of orthotoluidine.
(3) One of aniline and one of orthotoluidine.
(4) One of aniline and one of paratoluidine.
(5) One of orthotoluidine and one of para-

toluidine; but it does not take place with one molecule of paraphenylenediamine and two of paratoluidine (Witt, J. Soc. Chem. Ind. 1882, 256).

On the other hand, the other of the two molecules of monoamines must have a free ortho-position in order to be capable of entering the reaction. Thus the indamine of the above formula forms safranines with all the primary aromatic monoamines of the benzene series, with the exception of one xylidine and of mesidine, of the respective formulæ

CH_3⟨⟩CH_3 and CH_3⟨⟩CH_3
                   NH_3
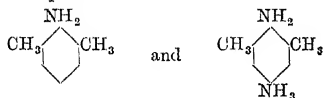
because these two have no free ortho- position to be used for the formation of the azonium group (Nietzki, Ber. 19, 3017 and 3136).

It is also necessary that this second molecule of monoamine be a primary base, whilst the one necessary for the formation of the indamine may be either primary, secondary, or tertiary, provided always that it possesses a free para-position.

6. It is evident that the general process described under 4 may be modified; thus, for instance, the dipara-amino- derivatives of secondary bases (being the leuco- compounds of indamines) may be oxidised together with one molecule of a primary aromatic monoamine, when a safranine is the result (see top of page, second column):

7. Another modification (Witt, Ber. 10, 873) consists in heating aminoazo- compounds with the hydrochlorides of aromatic monoamines.

This is the oldest process for the manufacture of safranines. The mechanism of this reaction is simple. Part of the aminoazo- compound being reduced, a mixture of a paradiamine and a primary monoamine in molecular proportions is formed, which with the monoamine added in the shape of hydrochloride, is transformed into safranine by the dehydrogenating action of the remaining part of the aminoazo- compound. It is evident that the yield must be small in this process of manufacture, and such is actually the case.

8. An asymmetrical safranine has obtained by the reduction of picryl-orthophenylenediamine (Kehrmann, Ber. 33, 3074).

9. Certain compounds belonging to the safranine group (mauveïne, &c.) are formed in a very complicated reaction by the oxidation of heavy aniline alone; on continued oxidation mauveïne is converted into a safranine (Perkin, Roy. Soc. Proc. 35, 717).

The following is an account of the more important and more thoroughly investigated safranines :—

A. MONAMINO- DERIVATIVES OF AZONIUM BASES.

1. **Aposafranine**, Monoaminophenylphenazonium chloride, has been obtained by Nietzki and Otto (Ber. 21, 1736; see also Annalen, 286, 188, and Ber. 30, 2624, and 33, 3078) from phenosafranine (see below) by diazotising one of its amino- groups, and eliminating it by means of alcohol. It is a red dyestuff of no practical importance, but very interesting as prototype of the induline group (see under INDULINES).

2. **Red dyestuff** $C_{22}H_{16}N_3Cl$. Obtained by the action of dichloroquinonimide on phenyl-β-naphthylamine, was prepared by Nietzki and Otto (Ber. 21, 1598) by heating the ingredients in molecular proportion in alcoholic solution on the water-bath. The nitrate forms green needles or prisms which are soluble in water with a magenta-red colour. The hydrochloride dissolves in sulphuric acid with a red colouration, which on dilution changes through green into red.

3. **Violet colouring matter** $C_{24}H_{20}N_3Cl$. Prepared by Witt (Ber. 21, 719) by acting with 3 molecules of nitrosodimethylaniline hydrochloride in an acetic acid solution on 2 molecules of phenyl-β-naphthylamine. This is the dimethyl- derivative of the preceding substance.

The hydrochloride forms large black needles soluble in water, with a fine violet colour. The free base, $C_{24}H_{20}N_3 \cdot OH$, is liberated from the salts by caustic alkalies only. It is insoluble in water, soluble in alcohol, with a red colour and a fine orange fluorescence. It is sold as ' neutral blue.'

4. **Violet colouring matter** $C_{25}H_{22}N_3Cl$. Prepared by Witt (Ber. 21, 719) from paratolyl β-naphthylamine in exactly the same manner as the preceding substance, of which this is the next homologue. Violet soft needles, resembling in their colour and reactions the phenyl-derivative.

The above substances have been patented (Otto N. Witt, D. R. P. 19224, dated Feb. 18, 1882).

5. **Basic blue** $C_{33}H_{29}N_4Cl$ is a fine blue dyestuff prepared (T. Annaheim, Ber. 20, 1371; Durand and Huguenin, Ger. Pat. 40886) by the reaction of nitrosodimethylaniline hydrochloride on the paratolylnaphthylenediamine which is formed by heating Ebert and Merz's dihydroxynaphthalene with paratoluidine hydrochloride. It forms a brown crystalline powder, soluble in water with a bluish-violet shade. In concentrated sulphuric acid it dissolves with a greenish-brown shade, which changes through green into violet on dilution.

6. **Azine green** $C_{30}H_{25}N_4Cl$ is formed by the reaction of nitrosodimethylaniline hydrochloride upon 2-6-diphenylnaphthylenediamine.

7. **Induline scarlet** $C_{19}H_{18}N_3Cl$, a very beautiful red dyestuff discovered by Schraube (D. R. P. 77226), and manufactured by the Badische Aniline and Soda-Fabrik, is really not an induline, but a safranine. It is prepared by melting together the hydrochloride of anilinazoethylparatoluidine and α-naphthylamine. The reaction is strictly analogous to the formation of the typical eurhodine.

B. DIAMINO- DERIVATIVES OF AZONIUM BASES.

1. **Phenosafranine** $C_{18}H_{15}N_4Cl$. Discovered by Witt (exhibited in Paris in 1878 ; and mentioned in the catalogue of Messrs. Williams, Thomas & Dower, closely investigated by Nietzki (Ber. 16, 464) and by Bindschedler (Ber. 13, 207 ; 16, 865).

It was with this compound that the mode of formation of the safranines and their chemical properties were definitely ascertained, chiefly by R. Nietzki, whose brilliant researches on this subject did much to clear up the chemistry of this group.

Phenosafranine is prepared by the joint oxidation of paraphenylenediamine and aniline. The mechanism of this process has already been discussed. A dilute aqueous solution of the normal hydrochlorides of these bases is used, and their oxidation is accomplished by adding potassium or sodium bichromate or manganese dioxide in the necessary proportion to the hot solution. The blue colour of the indamine which appears at first is immediately replaced by the red colour of the safranine formed. A certain quantity of insoluble dark by-products is always formed, but by careful work the yield of pure safranine may be raised to 70 p.c. of the theory. When the oxidation is finished, soda solution or chalk is added in order to precipitate the

impurities, and the liquid is filtered.[6] By adding a small amount of nitric acid and some sodium nitrate to the filtered solution, the nitrate of the safranine crystallises out ; or the chloride may be prepared by adding common salt to the solution after acidifying it with hydrochloric acid. By repeated recrystallisation from water or alcohol, the phenosafranine is obtained in a state of purity, in the form of magnificent green needles. The *sulphate* forms blue needles. The platinum salt $(C_{18}H_{15}N_4Cl)_2PtCl_4$ forms insoluble shining leaflets. Phenosafranine forms a diacetyl- derivative on boiling with acetic anhydride in the presence of dry sodium acetate. It forms two diazo-derivatives, of which the first

$$C_{18}H_{13}N_3Cl$$
$$\diagdown N : N \cdot Cl$$
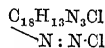
is rather stable and soluble in water, with blue colouration. The other diazo- compound

$$\diagup N : N \cdot Cl$$
$$C_{18}H_{11}N_2Cl$$
$$\diagdown N : N \cdot Cl$$
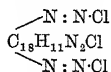
is very unstable and of a green colour.

Phenosafranine dyes wool, silk, and cotton a magnificent pink. Its aqueous solutions are red and show no fluorescence, whilst alcoholic solutions show a marked greenish-yellow fluorescence. Phenosafranine dissolves in concentrated sulphuric acid with a green colouration which changes through blue into red on dilution, thus indicating the actual existence of the three series of salts foreshadowed by theory.

If phenosafranine or its homologues be diazotised and then combined with β-naphthol, beautiful basic blue dyestuffs are obtained, which are largely prepared and used for cotton-dyeing and calico-printing under the name of ' Indoine blue.'

The alkyl- derivatives of phenosafranine are interesting colouring matters, some of which have found an industrial application. They have not been prepared by introducing alkyl-groups into ready-formed safranine, but rather by direct synthesis from suitable raw materials. Each of them exists in two isomeric modifications, according to the amino- group into which the alkyl- group has been introduced. The two amino- groups of phenosafranine being asymmetric, and therefore not equivalent to one another, must of necessity produce different products on being alkylated.

α-**Dimethylsafranine** $C_{20}H_{19}N_4Cl$ is produced by the simultaneous oxidation of one molecule of paraphenylenedimethyldiamine with two molecules of aniline.

It is a dyestuff of a magenta-red shade. Its nitrate crystallises in green needles (Bindschedler, Ber. 16, 869).

β-**Dimethylsafranine** is obtained by oxidising a mixture of one molecule of paraphenylenediamine with one molecule of aniline and one molecule of dimethylaniline. Its shade is similar to that of the preceding one ; its nitrate forms brown leaflets (Nietzki, Ber. 19, 3017 and 3136).

The two **diethylsafranines** are obtained in similar manner. Their chlorides form green needles which dissolve in water with a violet

shade (Nietzki, Ber. 16, 464). These substances, and especially the α- derivatives, are manufactured under the name of *Fuchsia*.

Tetramethylsafranine (Bindschedler, *l.c.*) and **tetraethylsafranine** (Nietzki, *l.c.*) may be prepared by the joint oxidation of one molecule of paraphenylenedimethyl- (or diethyl-) diamine with one molecule of aniline and one molecule of dimethyl- or diethylaniline. These substances have been sold under the name of *Amethyst*. Their shade is a magnificent violet, with a fine crimson fluorescence. Unfortunately, they are very fugitive.

2. **Tolusafranines** (Hofmann and Geyger, Ber. 5, 526, and very numerous other publications) $C_{21}H_{21}N_4Cl$. A mixture of the isomerides of this formula is the safranine of commerce. It is prepared by the oxidation of a mixture of paratolylenediamine with the two toluidines. This mixture is obtained by treating three molecules of the orthotoluidine of commerce (which contains from 6 to 10 p.c. of paratoluidine) with two molecules of hydrochloric acid and one molecule of sodium nitrite dissolved in as little water as possible. A thick heavy oil is the result, which is merely a solution of amino-azotoluene in the excess of toluidine present. By dissolving this oil in hydrochloric acid, and reducing it with either zinc-dust or iron borings, the amino-azo- compound is split up into paratolylenediamine and orthotoluidine; consequently, the aqueous liquid produced contains the bases in the necessary proportions for the production of safranine. The rest of the treatment is exactly similar to the one described for pheno-safranine. The safranine is precipitated from the liquid by the addition of salt. By redissolving it in water, boiling with a small quantity of potassium bichromate, treating it afresh with milk of lime or chalk, and reprecipitating the filtered liquid with clean salt, the safranine is purified so as to give the brightest shades on dyeing. Safranine prepared with a toluidine rich in paratoluidine is very insoluble in cold water, and therefore generally disliked by the dyer. The presence of aniline has not the same disagreeable effect: some manufacturers therefore use the first runnings of the magenta process, which consist of aniline and orthotoluidine, and contain no paratoluidine, as a suitable raw product for the manufacture of safranine. The safranine of commerce forms a brown powder which dissolves readily in hot water. It dyes a bluish-pink on textile fibres, and was chiefly used for dyeing cotton. The introduction of the so-called substantive azo- colours, derived from benzidine and its congeners, has much diminished the use of safranine.

3. **Girofle.** A dimethylphenoxylosafranine has been produced by heating nitrosodimethyl-aniline hydrochloride with xylidine, and sold under the above name as a violet colouring matter of a pleasing shade.

4. **Safranisol** $C_{18}H_{19}(OCH_3)_2N_4\cdot Cl$ is a substance which has been obtained by Nietzki by the joint oxidation of one molecule of para-phenylenediamine with two molecules of ortho-anisidine. It dyes a very beautiful yellowish-pink with a yellow fluorescence. This product has been patented (Kalle & Co., D. R. P. 24229), but owing to the high price of its production

it has been unable to compete with the eosin colours, which are perhaps still more brilliant in shade.

5. **Magdala red** $C_{30}H_{21}N_4Cl$. This old and very beautiful colouring matter is the safranine of the naphthalene series. It was discovered by Schiendl and first investigated by Hofmann (Ber. 2, 374), who, however, owing to the great difficulties of its analysis, assigned to it the erroneous formula $C_{30}H_{21}N_3\cdot HCl$. After a revision of the analytical data by Julius (Ber. 19, 1365), its true composition was established. This substance cannot be prepared by the usual oxidation process from paranaphthylene-diamine and naphthylamine because para-naphthylenediamine is at once transformed into α-naphthaquinone even by the feeblest oxidising agents. Magdala red has therefore to be prepared by the old process of heating α-amino-azonaphthalene with α-naphthylamine acetate. The chief product of this reaction is rhodindine, the induline of the naphthalene series (v. INDULINES); but a small proportion (6–8 p.c.) of Magdala red is formed at the same time. This is extracted from the melt by repeated treatment with boiling water, in which it is sparingly soluble. On cooling, this solution deposits the dyestuff in the shape of gelatinous flakes, It is purified by repeated crystallisations from water. When pure, it forms a dark crystalline powder, which dissolves in alcohol with a pink colour and a magnificent orange fluorescence. It is used for dyeing light pinks on silk, but is now rapidly being replaced by rhodamine (v. TRIPHENYLMETHANE COLOURING MATTERS). If ready-formed paranaphthylenediamine be added to the magenta-melt, the proportion of Magdala red formed is considerably increased (Otto N. Witt, D. R. P. 40868). It is thus shown that Magdala red is, after all, only a product of the joint oxidation of paranaphthylenediamine and α-naphthylamine.

The pure salts of Magdala red, when recrystallised from spirit, form green needles with a metallic lustre. The chloride, sulphate, picrate, and platinum double chloride have been prepared and analysed. These salts dissolve in concentrated sulphuric acid with a blue-black colour which changes into red on dilution.

Mixed Magdala reds have been prepared either by heating amino-azonaphthalene with aromatic monoamines of the benzene series (M. T. Lecco, Ber. 7, 1290), or by heating aminoazo-compounds of the benzene series with para-naphthylenediamine hydrochloride and aniline, toluidine, or even phenol (Otto N. Witt, D. R. P. 40868). These dyestuffs resemble Magdala red in their properties.

6. **Indazine** is the commercial name of a safranine dye, which is obtained by heating the symmetrical diphenylmetaphenylenediamine (prepared by heating resorcin with aniline hydrochloride in the presence of zinc chloride) with nitrosodimethylaniline hydrochloride. Its constitution may be inferred from its analogy to the violet dyestuff prepared from nitrosodimethylaniline and phenyl-β-naphthylamine. It is a serviceable blue, of considerable intensity, but little brilliancy of shade.

Mauveine $C_{27}H_{25}N_4Cl$. This substance, the oldest of all the artificial colouring matters, is still manufactured in a small way, and sold under

the name of rosolane. It was discovered and examined by W. H. Perkin (Roy. Soc. Proc. 35, 717), who also described the mode of its production. It is prepared by oxidising heavy aniline with potassium dichromate, and extracting the mauveïne formed with water or spirit from the black insoluble mass which is the chief product of the reaction. A dyestuff resembling mauveïne in all its properties may be prepared by the reaction of nitrosodiphenylamine on aniline (Otto Fischer and Hepp, Ber. 21, 2617) or by the joint oxidation of diphenylmetaphenylenediamine and paraphenylenediamine or meta-aminodiphenylamine and para-aminodiphenylamine. These syntheses are a clue to the constitution of mauveïne, which has been a mystery for nearly half a century—it stands revealed as phenylphenosafranine. The above synthetical methods have been adopted for the industrial preparation of mauveïne, as they give better yields than Perkin's old process of oxidation. Mauveïne is generally sold in the shape of a violet paste. It is insoluble in cold, sparingly soluble in hot water, easily soluble with a fine purple shade in spirit. Concentrated sulphuric acid dissolves it with an olive-green colouration, which on dilution with water changes through green and blue into purple. Mauveïne still holds its own against the cheaper new violets on account of its great fastness to light and other influences. It is used for shading the white in bleached silks, and also for printing on paper.

Mauveïne yields on oxidation a pink dyestuff which is supposed to be identical with ordinary phenosafranine. In our opinion this statement requires confirmation. O. N. W.

AZOBENZENE $C_{12}H_{10}N_2$. A product of the partial reduction of nitrobenzene, obtained by Mitscherlich (Annalen, 12, 311) by boiling an alcoholic solution of nitrobenzene with potash and distilling the product.

Preparation.—Azobenzene is obtained by acting with sodium amalgam (4–5 p.c. of sodium) on nitrobenzene dissolved in ether containing water (Werigo, Annalen, 135, 176; Alexejeff, J. 1864, 525; Rasenack, Ber. 5, 367); the product, according to Alexejeff (J. 1867, 503) is azobenzene or azoxybenzene, according as the sodium amalgam or nitrobenzene is in excess. On the large scale azobenzene is prepared by the reduction of nitrobenzene in alcoholic solution with zinc-dust and aqueous soda. In this reaction the reduction tends to go further, and some hydrazobenzene is also obtained; this, however, is readily oxidised to azobenzene if nitrous fumes are passed into the alcoholic solution of the product (Alexejeff, J. 1867, 503). Azobenzene can also be prepared by distilling azoxybenzene (1 part) with iron filings (3 parts) (Schmidt and Schultz, Ber. 12, 484); by heating nitrobenzene on a water-bath with the calculated quantity (2 mols.) of stannous chloride dissolved in excess of aqueous caustic soda (Witt, Ber. 18, 2912); by reducing nitrobenzene in alcoholic solution with magnesium amalgam (yield 95 p.c.) (Evans and Fetsch, J. Amer. Chem. Soc. 1904, 1158); by reducing nitrobenzene with alkali sulphide in the presence of alkali (Farb. vorm. Meister, Lucius, and Brüning, D. R. P. 216246, J. Soc. Chem. Ind. 1909, 1310); by heating nitrobenzene with charcoal and alkali (Farb.

vorm. Fried. Bayer & Co., D. R. P. 210806; Chem. Zentr. 1909, 2, 163); by treating phenylhydrazine with bleaching powder solution (Brunner and Pelet, Ber. 1897, 284). Azobenzene can be prepared by the electrolytic reduction of nitrobenzene in the presence of alkali (Elbs and Kopp, J. Soc. Chem. Ind. 1898, 1137; Löb, Ber. 1900, 2329; Farb. vorm. Fried. Bayer & Co., D. R. PP. 121899 and 121900; Chem. Zentr. 1901, 2, 153; Farb. vorm. Meister, Lucius and Brüning; D. R. P. 141535; Chem. Zentr. 1903, (i.) 1283; and Farb. vorm. Weiler-ter-Meer, D. R. P. 138496; Chem. Zentr. 1903, (i.) 372).

Properties.—Azobenzene crystallises in large yellowish-red crystals belonging to the monoclinic system (Boeris, R. Accad. Lincei, [5] 8, i. 575), and to the rhombic system (Alexejeff, Chem. Soc. Abstr. 42, 965); melts at 68°, boils at 293°, and is readily soluble in alcohol and ether, insoluble in water. From benzene it crystallises with benzene of crystallisation in rhombic prisms, which lose benzene on exposure to the air. Weak reducing agents, such as ammonium sulphide or zinc-dust in alkaline solution (Alexejeff, Annalen, 207, 327) or phenylhydrazine (Walther, J. pr. Chem. 1896, 54, 433), convert azobenzene into hydrazobenzene, but benzidine is obtained when stronger reducing agents such as sulphurous acid or hydrogen iodide are employed (Bordenstein, D. R. P. 172569; J. Soc. Chem. Ind. 1907, 272), or the alcoholic solution is treated in the cold with stannous chloride and a little sulphuric acid (Schultz, Ber. 17, 464: Mentha and Heumann, Ber. 19, 2970). Azobenzene can also be electrolytically reduced to benzidine (Löb, Ber. 1900, 2329; when heated with ammonium hydrogen sulphite and alcohol under pressure, it is converted into benzidine-sulphamic acid (Spiegel, Ber. 18, 1481). When melted with *p*-phenylenediamine in the presence of ammonium chloride, it yields a soluble induline dye (Farb. vorm. Fried. Bayer & Co., D. R. P. 53198; Ber. 1891, Ref. 137). Azobenzene yields a mixture of mono-, di-, and tri-nitroazobenzenes when treated with fuming nitric acid (Gerhardt and Laurent, Annalen, 75, 73; Janovsky and Erb, Ber. 18, 1133; 19, 2157; Janovsky, Monatsh. 7, 124; Werner and Stiasny, Ber. 1899, 3256): ordinary sulphuric acid dissolves it without alteration, whilst the fuming acid at 130° converts it into azobenzenemonosulphonic acid (Griess, Annalen, 154, 208; Janovsky, Monatsh. 2, 219); chromic acid oxidises it to carbon dioxide and nitrogen (De Coninck, Compt. rend. 1899, 128, 682). The bromine derivatives of azobenzene have been examined by Werigo (Annalen, 165, 189), Janovsky (*l.c.*), and Mills (Chem. Soc. Trans. 1894, 51).

AZOBENZENE RED *v.* AZO- COLOURING MATTERS.

AZO-BLACK or **NAPHTHOL BLACK** *v.* AZO-COLOURING MATTERS.

AZO-BLUE *v.* AZO- COLOURING MATTERS.

AZO-COCCINE *v.* AZO- COLOURING MATTERS.

AZO- COLOURING MATTERS.

History.—The colouring matters of this class contain one or more azo- groups—N : N—linking together aromatic radicles. The typical parent substance from which these compounds may be regarded as being derived is azobenzene

$C_6H_5 \cdot N : N \cdot C_6H_5$, which has been known since the year 1834 (Mitscherlich, Annalen, 12, 311). The basic and acid derivatives of azobenzene are all colouring matters, the amino- derivative, aminoazobenzene, having been the first of these compounds which was prepared and introduced into commerce on anything approaching a large scale by the firm of Simpson, Maule, and Nicholson in 1863. This substance was prepared by the action of nitrous gases on aniline dissolved in alcohol, and was known in the market by the name of 'aniline yellow,' the true constitution of the colour being at the time unknown. The introduction of the first azocolour into commerce is thus due to the firm above mentioned, although the production of the colour itself appears to have been previously observed by Mène (Compt. rend. 1861, 52, 311), Luthringer (Brevet d'invention, Aug. 30, 1861), and Griess (Annalen, 1862, 121, 262, note). The first researches on the diazo- compounds (as distinguished from azo- compounds) were published in 1858 by Griess (Annalen, 106, 123), who in 1862 discovered a compound produced by the action of nitrous acid on aniline, to which he gave the name of 'diazoamidobenzol' (Annalen, 131, 257). The latter was, however, a true diazo- compound, and on comparing it with the 'aniline yellow' of commerce it was found that the two substances were isomeric, a discovery which led to the establishment of the true formula of aminoazobenzene by Martius and Griess in 1866 (Zeitsch. Chem. N. F. 2, 132). In this same year a brown dye was sent into the market by the firm of Roberts, Dale, and Co., of Manchester, and this colouring matter (known as Manchester Brown, Vesuvine, Phenylene Brown, or, more generally, Bismarck Brown) was investigated by Caro and Griess, and identified as an azo- compound in 1867 (Zeitsch. Chem. N. F. 3, 278). These chemists regarded it as triaminoazobenzene, but G. Schultz (Chemie des Steinkohlentheers, 2nd ed. 2, 193) showed that it is benzene-1 : 3-disazophenylenediamine. This compound still occupies an important place in the tinctorial industries, whilst the earlier known aminoazobenzene (aniline yellow) has been completely abandoned on account of its fugitive character. It is, however, used in the preparation of other azocolouring matters and indulines. In 1876 a beautifully crystalline orange colouring matter made its appearance as a commercial product under the name of 'chrysoïdine,' its composition and constitution having been established by Hofmann (Ber. 1877, 10, 213), who showed that it was diaminoazobenzene. This colouring matter was discovered almost simultaneously by Caro and Witt, independently, in 1876, but was first introduced into commerce by the latter, the manufacture having been carried out by the firm of Williams, Thomas, and Dower, of Brentford and Fulham.

The manufacture of chrysoïdine was the first industrial application of Griess's discovery of the diazo- compounds, the colouring matter in question being prepared by the action of a diazosalt (diazobenzene chloride) on m-phenylenediamine, and this manufacture was soon followed by the appearance of acid azo- compounds prepared by the action of diazosulphonic acids on phenols. The typical parent substance

of these acid azo- colours may be regarded as hydroxyazobenzene, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot OH$, which was first prepared by Griess in 1864 (Phil. Trans. 153, 679). The general method by which the azo- colours are now prepared is an application of the reaction between diazo- salts and phenols in alkaline solution, first made known by Kekulé and Hidegh (Ber. 1870, 3, 233), the first colouring matters of this class having been introduced by Witt under the name of 'Tropæolines' (Chem. Soc. Trans. 1879, 35, 179), and simultaneously by Poirrier, of St. Denis, under the designation of 'Orange' of various brands. Since the first appearance of the acid azo- colours immense numbers of these compounds have been sent into commerce under various designations, the first patent having been taken out by Griess in 1877 (E. P. 3698), and being quickly followed by others, which will be referred to in due order. Of the acid azo- colours described in the earlier specifications, the most successful from an industrial point of view were those manufactured by the 'Badische Anilin- und Soda-Fabrik' (Ber. 1879, 12, 1364), and by Meister, Lucius, und Brüning, of Höchst (ibid. 144).

The next step of importance in the industrial history of the azo- colours was the introduction of disazo- compounds, containing two azo- groups. The typical compound of this class is benzeneazobenzeneazophenol $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH$, discovered in 1877 by Caro and Schraube (Ber. 10, 2230). In 1879 appeared the 'Biebrich scarlet' of Nietzki (Ber. 1880, 13, 800, 1838), which was introduced by the firm of Kalle & Co. of Biebrich. This dyestuff is prepared by combining diazotised aminoazobenzenedisulphonic acid with β-naphthol, and was the first of the secondary disazo- compounds. The first primary disazo- colouring matter, 'Rescrcin brown,' was discovered in 1881 by Wallach, who combined two molecules of a diazo- compound (m-xylidine and sulphanilic acid) with one molecule of a phenol (resorcinol). In 1884 a very important discovery in the history of azocolouring matters was made by P. Böttiger, who found that the disazo- compound obtained by combining the tetrazo- salt prepared from benzidine with naphthionic acid possessed the valuable property of dyeing cotton direct, without the use of a mordant. This colouring matter was put on the market by the Aktiengesellschaft für Anilinfabrikation, under the name of 'Congo red.' This discovery has given rise to the production of a very large number of similarly constituted colouring matters, which appear on the market under the names of benzo-, Congo-, diamine-, and other dyestuffs. In the following year another important development was announced by the introduction of the first satisfactory black azo- colouring matter (naphthol black) for wool. This was discovered by Hoffmann and Weinberg, and placed on the market by L. Cassella & Co. In 1887 A. G. Green found that primuline, which he had discovered, dyed cotton direct, and that the yellow colouring matter when thus dyed on the fibre, could be diazotised and combined (developed) with β-naphthol, m-phenylenediamine, and similar 'developers,' thus giving rise to a series of new azo- dyestuffs (Ingrain colours). This discovery led to the manufacture of many azocolouring matters which were capable of being

similarly diatotised and developed on the fibre (*e.g.* diamine black), as also to the production of azo- colouring matters on the fibre by treating the fibre already dyed with an azo- colour with a diazo- compound (*e.g.* benzonitrol colours). In both cases darker and faster dyeings are obtained.

The first direct cotton black (diamine black, R.O) was discovered in 1889 by Gans (Cassella & Co.), and in 1891 Hoffmann and Daimler prepared the first green colouring matter of this kind (diamine green).

A modified method of the process introduced in 1880 by Read Holliday and Sons, of producing insoluble azo- colouring matters directly on the fibre, has been largely developed of late years. The first example of this, viz. the combination of diazotised *p*-nitroaniline with β-naphthol (' paranitraniline red ') still holds the place of greatest importance.

Manufacture.—The general method of preparing the azo- colours on a large scale depends upon the reaction between a diazo- salt, usually the chloride, and a phenol or phenolsulphonic acid in presence of an alkali, as typified by the following example :—

$C_6H_5 \cdot N_2Cl + C_6H_5 \cdot ONa$
Diazobenzene   Sodium
chloride.   phenoxide.
$= C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot OH + NaCl.$
Benzeneazophenol.
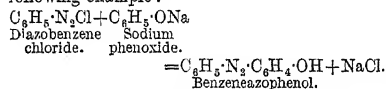
Aminosulphonic acids or aminocarboxylic acids when diazotised react in a similar manner :

$$C_6H_4 {<}{\stackrel{N_2}{SO_3}}{>} + C_6H_5 \cdot ONa$$
Diazosulphanilic   Sodium
acid.   phenoxide.
$= SO_3Na \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH.$
Sulphobenzeneazophenol (sodium salt).
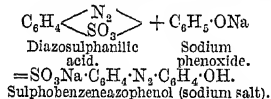
Preparation of the diazo- salts.—The amine to be diazotised is usually dissolved in about 10 parts of water and one equivalent of hydrochloric (more rarely sulphuric) acid. For diamines twice this amount of acid is taken. The solution[1] is now cooled by adding ice until the temperature is, in the case of aniline, the toluidines, the xylidines, &c., 0°–2°, or, in the case of the naphthylamines, the nitroanilines and diamines such as benzidine, tolidine, dianisidine, &c., 5°–10°. This is done by adding ice to the solution. More acid (1½–2 equivalents) is now added (or 3–4 in the case of diamines), and a solution of the calculated quantity of sodium nitrite is run in, sufficient being used to give a reaction with starch-iodide paper after the whole has been mixed for two or three minutes. (For velocity of diazotisation, *see* Hantzsch and Schumann, Ber. 1899, 32, 1691 ; Schumann, *ibid.* 1900, 33, 527.) In certain cases (*e.g. a*-naphthylamine, *p*-nitroaniline, &c.) it is better to add the nitrite all at once in order to avoid the formation of the diazoamino- compound. In diazotising such compounds as give an insoluble diazo- derivative, as, for example, *p*-sulphobenzeneazo-*a*-naphthylamine or *p*-acetylaminobenzeneazo-*a*-naphthylamine, and which themselves are insoluble in acids (under the above conditions) it is advisable to use an excess of nitrite and to stir the ice-

old mixture for several hours. Special methods have to be employed to diazotise amines containing several negative groups ; the operation may often be effected by carrying it out in the presence of excess of 50 p.c. sulphuric acid, and Witt has shown (Ber. 1909, 42, 2953) that diazotisation is easily brought about in these cases by employing strong nitric acid. Other substances which are difficult to diazotise satisfactorily are those which are readily oxidised by the nitrous acid, such as the 1 : 2- and the 2 : 1-aminonaphthols and their sulphonic acids. In this case the diazotisation may be done in the presence of zinc or copper salts (compare E. P. 10235 of 1904 ; D. R. P. 171024, 172446 ; E. P. 353786) or by means of zinc nitrite. Another method is to diazotise in presence of an excess of acetic or oxalic acid (compare D. R. P. 155083, 175593, also E. P. 2946 of 1896).

Difficulties are often encountered in endeavouring to diazotise certain diamines. *o*-Phenylene- and tolylene-diamines cannot be diazotised, as they yield the azimino- derivatives, and, under the usual conditions, the metadiamines furnish Bismarck brown ; but if the diamine is run into a mixture of nitrite and acid the tetrazo- compound may be obtained (Griess, Ber. 1886, 19, 317 ; Täuber and Walder, Ber. 1897, 30, 2901 ; E. P. 1593 of 1888 ; D. R. P. 103685). In the case of *p*-phenylenediamine and certain diamines of the naphthalene series diazotisation is brought about indirectly, as the direct action of nitrous acid often leads to a mixture of the mono- with the bis-diazo- (or tetrazo-) compound. Either the corresponding nitroamine or the monoacetylated diamine is employed. This is diazotised and combined with a component in the usual way (*see* below), and then the nitro- group is reduced or the acetyl group hydrolysed when the free amino- group can then readily be diazotised. Some diamines, indeed, can only be diazotised as regards one amino- group, the other being quite unattacked. In such cases (*e.g.* o-nitro-*p*-phenylenediamine, 1 : 4-naphthylenediamine-2-sulphonic acid—the latter being diazotisable only in acetic or oxalic acid solution) the monodiazo-salt is combined with a component and then the remaining amino- group, which before resisted all attempts at diazotisation, is easily diazotised (compare Bülow, Ber. 1896, 29, 2285 ; E. P. 2946 of 1896). (For further information on this subject, see Cain, The Chemistry of the Diazo- Compounds, Arnold, 1908.)

Combination (*coupling*) *of the diazo- compound with a component* (*phenol or amine*) *to form an azo- dyestuff.*—Before the diazo- solution is prepared a solution of a phenol or amine is made ready so that no delay may occur before coupling takes place. As a general rule, phenols are combined in alkaline and amines in acid (acetic) solution. In the case of phenols or naphthols the substance is first dissolved in the calculated amount of sodium hydroxide, the solution diluted with water, and sodium carbonate added in sufficient quantity to ensure an alkaline reaction being obtained at the end of the combination (*i.e.* a little more than one molecule of sodium carbonate to each molecule of hydrochloric acid, so that sodium hydrogen carbonate may be formed). When phenolic sulphonic acids

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[1] Some of the diazosulphonic acids, such as diazo-naphthionic acid, are insoluble in water, and are therefore employed in a state of suspension.

are the components, they may be dissolved in sodium carbonate instead of hydroxide. The phenolic solution, having been cooled to about 10°, is now ready, and the diazo- solution is run in gradually with constant stirring. Combination takes place at once,[1] and when all the diazo- solution has been added, the mixture must be tested to ensure an alkaline reaction, and the presence of a slight excess of the phenol (about 2–5 p.c. excess of the theoretical amount is usually taken). The next day the colouring matter is filtered through filter presses. If it has separated out, no further treatment is necessary, but if it is still partly or wholly in solution, it is 'salted out' (hot or cold) by adding common salt until a spot on filter paper shows only a faintly coloured rim. In rare cases the precipitation is effected by acidifying. The filtration is best effected by the aid of compressed air and the press cake is spread on trays and dried. The dry lumps are then ground in a mill, adjusted to 'type' or 'standard' by means of common salt, sodium sulphate, &c., and the product is then ready for the market. In cases where the possibility of the formation of a disazo- dyestuff is present (dihydroxy- compounds, α-naphthol, &c.), the coupling may advantageously be carried out in acetic acid solution.

The procedure adopted in the case of amines is very similar to the above. The amine is first dissolved in the appropriate amount of hydrochloric acid, the solution diluted and sufficient sodium acetate added to ensure that no free mineral acid remains at the end of the combination (in rare cases coupling is effected in mineral acid or alkaline solution). When the combination is complete, the dyestuff is filtered off either as it is or after having been rendered alkaline.

Many disazo- dyestuffs are prepared by combining two molecules of the same or different diazo- compounds with an aminonaphtholsulphonic acid. In this case combination is effected first in acid solution and then the monoazo- dyestuff thus formed is rendered alkaline, and the second molecule of diazo- compound added.

Position assumed by the azo- group in the formation of azo- colouring matters.—(a) *Benzene series* : When the para- position with respect to the amino- or hydroxy- group is occupied by a hydrogen atom, and no group, such as NO_2, SO_3H, or NR_3Cl, is in the meta- position, the azo- group enters the para- position in place of the hydrogen atom. (b) *Naphthalene series* : In corresponding compounds of the naphthalene series (α-naphthylamine, α-naphthol) the entering azo- group also takes up the para- position, but when, in α-naphthol, a sulphonic group is in the 3- or 5-position with respect to the hydroxy- group, or a nitro- or NR_3Cl- group is in the 3- position, the azo- group enters the 2- position.

When the para- position is substituted, the azo- group enters the ortho-(2)- position, but if the para- substituent is a carboxy- group, this is usually displaced by the azo- group.

When diazo- compounds act on β-naphthylamine or β-naphthol, the azo- group enters

[1] For the formation of diazo-oxy- compounds, *see* paper by Dimroth and Hartmann, Ber. 1908, 41, 4012.

position 1 (in the ortho- position with respect to the amino- or hydroxy- group). When the 1- position in β-naphthol is occupied by a carboxy- group, this is displaced (compare also Scharwin and Kaljanoff, Ber. 1908, 41, 2056 and article on DISAZO- and TETRAZO- COLOURING MATTERS).

Differing capacity for combination.—As will have been gathered from the preceding paragraph, the azo- group never enters the meta- position with respect to an amino- or hydroxy- group. Further, a component in which the para- position is occupied by a substituent group is not so readily attacked (in the ortho- position) as one that is not substituted (when the azo- group enters the para- position). Moreover, the capacity for combination depends also on the kind of diazo- compound employed, thus 2-naphthol-8-sulphonic acid and 2-naphthol-6-sulphonic acid in dilute solution do not combine at all with diazotised xylidine or naphthylamine, whilst diazotised aniline, aminoazobenzene, aminoazobenzenesulphonic acid and naphthylaminesulphonic acids couple easily with them. The combination with diazotised xylidine and naphthylamine can, however, be made to take place in concentrated solution. The diazo- compound of *p*-nitroaniline, in most cases, combines with extreme ease. Finally, 2-naphthylamine-6 : 8-disulphonic acid does not combine with any diazo- compound. (For measurement of the rate of formation of dyestuffs, *see* Goldschmidt, Ber. 1897, 30, 670, 2075; 1899, 32, 355; 1900, 33, 893; 1902, 35, 3534; Veley, Trans. Chem. Soc. 1909, 95, 1186.)

Considering now the formation of azodyestuffs from tetratozised diamines, it should be noted that diamines of the type of benzidine furnish tetrazo- compounds which can either be combined with two molecules of one component (phenol or amine) or with one molecule each of two components, and the reaction can thus be divided into two stages. This holds good even when one component only is used; thus tetrazotised benzidine combines almost at once with one molecule of naphthionic acid, forming a so-called intermediate product ; but the second molecule of naphthionic acid combines with this only slowly. Here also a difference in combining power is to be noted, thus tetrazotised benzidine combines more readily than does the corresponding compound from tolidine.

General properties.—(1) *Action of alkalis.* Hydroxyazo- dyes containing a sulphonic or carboxylic group usually form differently coloured salts, and consequently the addition of sodium hydroxide to their solutions produces a modification in the shade (compare Hewitt and Mitchell, Trans. 1907, 91, 1251). The isomeric colouring matters prepared from α- and β-naphthol show a characteristic difference in that only those derived from the former are changed by sodium hydroxide (*e.g.* benzoazurine, &c.).

(2) *Action of cold dilute acids.* Dyestuffs containing amino- or substituted amino- groups generally undergo a change when treated with dilute acid (compare Fox and Hewitt, Trans. 1908, 93, 333 ; Hewitt and Thomas, *ibid.* 1909, 95, 1292 ; Hewitt and Thole, *ibid.* 1909, 95, 1393 ; 1910, 97, 511). In the case of Congo

red and methyl orange this change is so profound that these colouring matters can be used as indicators.

(3) *Action of cold concentrated sulphuric acid.* Nearly all azo- colouring matters give characteristic colour changes with this reagent, and it is often used as an aid in the detection of dyes. Mixtures of dyes, when covered with sulphuric acid, often reveal themselves by the various colours produced by the particles as they become dissolved. There are certain relationships between the colour of the solution of azo- dyes in sulphuric acid, and therefore of their absorption spectra and their chemical constitution. Thus the dyestuff from aminoazobenzenesulphonic acid and β-naphthol gives a green colour, those from the same (diazotised) amine and β-naphtholsulphonic acids, a blue, and those from aminoazobenzene and its homologues combined with β-naphtholsulphonic acids a red violet (compare Ber. 1880, 13, 1840 ; Vogel, Sitzungsber. K. Akad. Berlin, 1887, 34, 715 ; Ber. 1889, 22, 634, 2062 ; Schütze, Zeitsch. physikal. Chem. 1892, 9, 2 ; Grebe, Diss. Leipzig, 1892).

(4) *Action of hot hydrochloric acid.* Certain azo- colouring matters, such as, for example, aminoazobenzene, are decomposed when boiled with concentrated hydrochloric acid ; reduction and oxidation take place accompanied by chlorination. In the instance quoted phenylenediamine, aniline, and benzoquinone or its chloro- derivatives are produced (Wallach and Kölliker, Ber. 1884, 17, 395).

(5) *Action of hot sulphuric acid* (Witt, Ber. 1887, 20, 571). Azo- colouring matters which are derived from phenyl- or tolyl-β-naphthylamine by the action of diazo- compounds on these bases, when boiled with moderately dilute sulphuric acid, yield the bases, or their sulphonic acids, from which the diazo- compound was prepared, together with naphthazines. Thus the dyestuff obtained by combining diazotised sulphanilic acid with phenyl-β-naphthylamine, is decomposed into sulphanilic acid and phenonaphthazine :

$$SO_3H·C_6H_4·N_2·C_{10}H_6·NH·C_6H_5$$

$$=SO_3H·C_6H_4·NH_2+C_{10}H_6\diagup_{N}^{N}\diagdown C_6H_4.$$
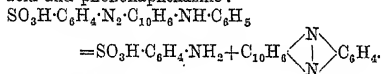
(6) *Action of nitric acid.* Azo- colouring matters are readily attacked by nitric acid, and the course of the reaction depends largely on the conditions of temperature and concentration. By the moderate action of nitric acid, the dyestuff may simply be nitrated, thus diphenylamine orange yields curcumeïne and, by further action, azo- acid yellow, the dyestuffs in both cases, however, being accompanied by some nitrodiphenylamine produced by the fission of the azo- group. Also when flavazol (diazotised toluidine combined with salicylic acid) is nitrated, it yields Persian yellow (*o*-nitrotolueneazosalicylic acid) (compare Ber. 1906, 40, 4207).

Methyl orange is decomposed even by cold dilute nitric acid ; a methyl group is eliminated in the process, and dinitromonomethylaniline is produced. The presence of a diazo- compound can also be detected (Fox, Ber. 1908, 41, 1989).

Cold fuming nitric acid decomposes many azo- colouring matters (particularly those containing an amino- or hydroxy- group in the para- position with respect to the azo- group), with the production of the diazo- compound from which the dye is prepared and the nitroderivative of the other component ; thus, orange II yields diazotised sulphanilic acid, and a nitro- derivative of β-naphthol and methyl orange gives *op*-dinitrodimethylaniline, tetranitrodimethylaniline and diazotised sulphanilic acid (O. Schmidt, Ber. 1905, 38, 3201).

Finally, warm nitric acid usually decomposes azo- dyestuffs, with the production of nitrophenols or bases.

(7) *Action of chlorine and bromine.* All azocolouring matters are readily attacked by chlorine or bromine. Fission generally takes place at the azo- group with the production of halogenated phenols, but some dyestuffs are converted into substitution products (compare Ber. 1884, 17, 272).

(8) *Action of reducing agents.* Reducing agents, such as zinc-dust and water, zinc-dust and ammonia, or sodium hydroxide, zinc-dust and dilute acids, tin and hydrochloric acid, stannous chloride and sodium hyposulphite (technically known as 'hydrosulphite') (Grandmougin, Ber. 1906, 39, 2494, 3561, 3929 ; compare also J. pr. Chem. 1907, (ii.) 76, 124 ; Franzen and Stickdorf, J. pr. Chem. 1907, (ii.) 76, 467 : O. Fischer, Fritzen and Eilles, J. pr. Chem. 1909, (ii.) 79, 562) attack the azogroup and convert it into two amino- groups ; thus :

$$NH_2·C_6H_4·N : N·C_6H_5+2H_2$$
$$=NH_2·C_6H_4·NH_2+C_6H_5·NH_2.$$
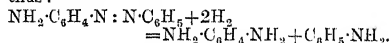
The base which was used to provide the diazocompound is thus regenerated, whilst the other component is converted into its amino- derivative.

By careful reduction with zinc-dust, dyestuffs obtained by the combination of diazotised aminoazobenzenesulphonic acid with phenols yield the aminoazosulphonic acid without the latter undergoing reduction. Further, nitroazo- dyestuffs can be reduced to the corresponding aminoazo- dyestuffs with sodium sulphide. The reduction of azo- dyestuffs is a useful means of attacking the problem of their constitution, although the operation requires considerable care (compare Witt, Ber. 1886, 19, 1719 ; 1888, 21, 3468, and especially the references quoted in connection with reduction by hydrosulphite).

Azo- dyestuffs are also readily reduced by titanous chloride, and a process for their estimation by titration with this reagent has been worked out by Knecht (J. Soc. Dyers, 1903, 19, 169 ; Ber. 1903, 36, 166, 1549 ; 1907, 40, 3819). A detailed account of the method of carrying out this and other methods of reduction will be found in Hans Meyer's Analyse und Konstitutionsermittelung organische Verbindungen, 2te aufl. 1909, p. 870.

(9) *Identification of azo- colouring matters on the fibre.* This is carried out by observing the action on the dyed fabric of various reagents, for which various tables have been constructed (compare Cain and Thorpe, The Synthetic Dyestuffs, 1905 ; Lunge, Chemisch-technische Untersuchungsmethoden, Eng. trans., edited by Keane, 1911).

Direct formation of azo- colours in the fibre.—
The production of an insoluble azo- dyestuff in

the fibre was first achieved by T. and R. Holliday (E. P. 2757 of 1880), who impregnated the fibre with α- or β-naphthol, passed it then through a diazo- solution, and finally developed the colour by treatment with alkali. An improvement on this process was introduced by the Farbwerke vormals Meister, Lucius und Brüning, in 1889, which consisted in 'padding' the fibre (generally cotton) with the sodium salt of a phenol (usually β-naphthol), and passing the cloth through a diazo- solution, the free mineral acid of which has been neutralised by adding sodium acetate. This process is very largely used at the present day, and is applied to the greatest extent to the production of the so-called 'para-red' (the azo- colour obtained by combining diazotised p-nitraniline with β-naphthol). The colouring matters produced in this way will now be described.

Paranitraniline Red. The colouring matter was first prepared in substance by Meldola (Chem. Soc. Trans. 1885, 47, 657) by combining diazotised p-nitroaniline with β-naphthol in alkaline solution. As stated above, it is now almost entirely produced on the fibre. The goods are soaked in a bath containing sodium β-naphthoxide and Turkey-red oil, or thickening materials, squeezed out and dried at 65°–80°. They are then passed through the diazo- solution, washed and soaped. In order to avoid preparing the diazo- solution in the dye-house, various preparations may be used. Thus, **Paranitraniline extra N** paste is a mixture of p-nitroaniline with the calculated amount of sodium nitrite, and needs only to be stirred slowly into the necessary quantity of hydrochloric or sulphuric acid, ice, and water, to produce the diazo-solution. A similar product is **Benzonitrol** paste. Other preparations contain the diazo-compound in a suitable form for keeping. Thus, **Nitrosamine Red** is the sodium salt of p-nitroantidiazobenzene (which is very stable) and furnishes the true diazo- solution when mixed with dilute acid. **Azophor Red, Azogen Red** and **Nitrazol C.** are mixtures of the diazo-sulphate with sodium sulphate (whereby sodium hydrogen sulphate is produced); they are dissolved in water, the solution filtered, if necessary, and neutralised before use with sodium acetate or hydroxide. Paranitraniline red is used as a substitute for the red Congo dyestuffs and for Turkey red. It is extracted from the fibre when treated with organic solvents, and when the fibre is heated to 180°–200° the dyestuff partly sublimes. (For the formation of paranitraniline red, *see* Pomeranz, Zeitsch. Farben. Ind. 1906, 5, 184; Erban and Mebus, Chem. Zeit. 1907, 31, 663, 678, 687; Lichtenstein, Zeitsch. Elektrochem. 1908, 14, 586; Prud'homme and Colin, Rev. Gen. Mat. Col. 1909, 13, 1, 66; Bull. Soc. chim. 1909, (iv.) 5, 779; Bucherer, and Wolff, Zeitsch. angew. Chem. 1909, 22, 731; Justin-Mueller, Bull. Soc. chim. 1910, (iv.) 7, 60.)

Metanitraniline Orange and **Nitro-o-toluidine Orange.** Prepared as above from diazotised m-nitroaniline or nitro-o-toluidine and β-naphthol. The former gives yellowish and the latter reddish shades of orange. Their use is not very extensive, as they are not fast to rubbing, and the colours sublime on keeping. An orange free from these disadvantages can, however, be obtained by using m-nitro-p-phenetidine.

Nitrophenetidine Rose or **Blue-red.** Here -nitro-p-phenetidine is used as the diazotised base. A substitute for this is **Azophor Rose A**, which is a mixture of a 'stable' diazo- compound with β-naphthol. Other rose shades are produced by the use of p-nitro-o-anisidine.

Naphthylamine Bordeaux. Prepared on the fibre from diazotised α-naphthylamine and β-naphthol. The dyestuff is used also as a pigment colour under the names **Carminaph :arnet (D. H.**[1]**)** and **Cerotine Scarlet 2 R** (C. J.).

Azo Turkey Red is produced by treating cloth padded with β-naphthol with diazotised β-naphthylamine. It is a bright scarlet, which, however, is not very fast.

Fast Azo Garnet. Prepared from diazotised o-aminoazotoluene and β-naphthol. It is also manufactured in substance and is used for colouring oils and varnishes under the names **Oil Scarlet** (M) (K) (W), **Red B, Oil soluble, extra conc.** (Remy), **Cerotine Ponceau 3 B** (C. J.), and **Fat Ponceau R** (K).

Benzidine and **Tolidine Puce.** Obtained from tetrazotised benzidine or tolidine and β-naphthol. Dark garnet to brown shades are produced which, however, are not fast to light. Rather yellower shades result by using tetrazotised diaminocarbazole instead of these diamines; when treated with copper salts the tints are very fast to light.

Dianisidine Blue. Tetrazotised dianisidine is combined on the fibre with β-naphthol in presence of copper salts. The tetrazo-compound is also put on the market as **Azophor Blue D**, a mixture of the tetrazo- compound and aluminium sulphate which has been dried in a vacuum at 45°. The colour is very fast to light, soap, and rubbing.

The production of black insoluble colours in the fibre was first effected by the Farbwerke vorm. Meister, Lucius und Brüning. The cloth is padded with β-naphthol and tragacanth, and treated with a mixture of the tetrazo-compounds of dianisidine and certain other bases. The mixture of bases sold for this purpose is known as **Azo Black Base O**, and the diazo- compounds are put on the market under the name of **Azophor Black S.** Cassella & Co. have introduced a black obtained by padding the cloth with 1 : 6- or 1 : 7-aminonaphthol, and then passing it through diazotised p-nitro-aniline so as to form the disazo- colouring matter. The aminonaphthol is put on the market as **Amidonaphthol BD** and **3 B**, and both brands are mixtures of the two aminonaphthols mentioned. Full black colours are obtained which are fast to soap and chlorine, but they are not very easily applied in printing. A black, also introduced by the same firm, is produced from **Azotol C**, which is an asymmetric dialkylated di-p-diaminoazobenzene (it is identical with Kinzlberger's **Ice Black**). The base is diazotised and combined with β-naphthol on the fibre in the usual way. The latter firm also has introduced the use of the diazo- compound of aminochrysoïdine, and of the tetrazo- compound of pp-diaminodiphenylamine for the production of black colours. Other tetrazo-compounds recommended are these of amino-benzene-azo-α-naphthylamine (By.) and diamino-dimethylcarbazole (M.).

[1] See p. 364 for the full names of firms of which these letters are a contraction.

Another process of producing azo- colouring matters on the fibre is by the use of primuline (*q.v.*). When cotton dyed with this dyestuff is treated with a solution containing hydrochloric acid and sodium nitrite, the dyestuff is diazotised. The cloth is now passed through a bath containing the ' developer,' consisting of a solution of an amine or a phenol. β-naphthol is mostly used in giving **Ingrain-** or **Primuline Red.** An orange colour is obtained with resorcinol (**Ingrain Orange**), and a brown with *m*-phenylenediamine (**Ingrain Brown**). Many direct-dyeing cotton colours which contain a diazotisable amino- group (for example, diamine black BH) acquire a faster, deeper, and modified shade when similarly diazotised on the fibre and developed with β-naphthol or *m*-phenylenediamine.

In the succeeding portion of this article it is proposed to give an account of the most important azo- colours which are at present in commerce.[1] Each colour will be treated of under its commercial name ; its chemical formula given, and the mode of preparation and general properties briefly described.

Unless otherwise stated, it may be assumed that azo- colouring matters containing a sulphonic or carboxylic group are placed on the market in the form of their sodium salts.

The following abbreviations are used for the names of firms :—

(A.) = Aktiengesellschaft für Anilinfabrikation, Berlin.

(B.) = Badische Anilin- und Soda-Fabrik, Ludwigshafen a/Rhein.

(Bl.) = The Basle Chemical Company.

(By.) = Farbenfabriken vorm. Fr. Bayer & Co., Elberfeld.

(C.) = Leopold Cassella & Co., Frankfurt a/Main.

(C. J.) = Carl Jäger, G. m. b. H., Düsseldorf-Derendorf.

(Cl. Co.) = The Clayton Aniline Co., Ltd., Clayton, Manchester.

(Claus & Co.) = Claus & Co., Clayton, Manchester.

(D.) = Dahl & Co., Barmen.

(D. H.) = Dye Works, formerly L. Durand, Huguenin, & Co., Basle.

(F.) = A. Fischesser & Co., Lutterbach.

(G.) = Aniline Colour- and Extract-Works, formerly John R. Geigy, Basle.

(H.) = Read Holliday and Sons, Ltd., Huddersfield.

(I.) = Société pour l'Industrie Chimique, (formerly Bindschedler und Busch), Basle.

(K.) = Kalle & Co., Biebrich a/Rhein.

(K. S.) = Sandoz & Co. (formerly Kern and Sandoz), Basle.

(L.) = Farbwerk Mülheim (formerly A. Leonhardt & Co.), Mülheim, near Frankfurt.

(Lev.) = Levinstein, Ltd., Blackley, Manchester.

(M.) = Farbwerke vorm. Meister, Lucius, und Brüning, Höchst a/Main.

(N. I.) = Farbwerk Griesheim, Nötzel, Istel & Co., Griesheim a/Main.

(O.) = Chemische Fabrik Griesheim-Elektron, Werk Oehler (formerly K. Oehler), Griesheim.

(P.) = Société Anonyme des Matières Colorantes & Produits Chimiques de St. Denis, Paris.

(P. L.) = Pick, Lange & Co., Amsterdam.

(Sch.) = The Schöllkopf Aniline and Chemical Company, Buffalo, U.S.A.

(T. M.) = Chemische Fabriken vorm. Weiler ter Meer, Uerdingen a/Rhein.

(W.) = Williams Bros. & Co., Hounslow, Middlesex.

Also E. P. = English Patent ; D. R. P. = German Patent ; F. P. = French Patent ; A. P. = American Patent.

I. BASIC AZO- COMPOUNDS.

Aniline Yellow ; Aminoazobenzene

$$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NH_2.$$
$$\quad [1] \qquad\qquad [4]$$
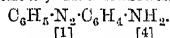
This compound, discovered by Mène in 1861 (Jahresber. p. 496), and introduced into commerce by Simpson, Maule, and Nicholson in 1863, is interesting as being the first azo- colour made on a manufacturing scale. It was formerly prepared by passing nitrous acid gas into an alcoholic solution of aniline. As a colouring matter it is now of no importance, but is largely used as the starting-point in the manufacture of other azo- colours and of indulines. In practice this compound cannot be prepared directly by the action of one molecule of nitrous acid on two molecules of aniline, since diazoaminobenzene is always the first product of this reaction :

$$2C_6H_5 \cdot NH_2, HCl + NaNO_2$$
$$= C_6H_5 \cdot N_2 \cdot NH \cdot C_6H_5 + NaCl + HCl + 2H_2O.$$
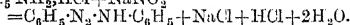
The diazo- compound is slowly converted into the isomeric aniline yellow on being kept for some time ·in contact with aniline and an aniline salt :

$$C_6H_5 \cdot N_2 \cdot NH \cdot C_6H_5 = C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NH_2.$$
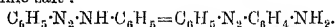
The manufacture is carried out as follows : 100 kilos. of aniline are mixed with 36 kilos. of concentrated hydrochloric acid, the mixture cooled (from outside) to about 18°, and a solution of 15·5 kilos. of sodium nitrite in 18 kilos. of water and 18 kilos. of saturated sodium chloride solution added at first fairly rapidly, so that the temperature rises to 25°, and then more slowly, the temperature being kept below 28° by outside cooling. This operation takes about 7–8 hours. After 24 hours the change of diazoaminobenzene into aminoazobenzene is complete. The salt solution is now drawn off, the residue stirred with 96 kilos. of hydrochloric acid and 64 kilos. of water, and the aminoazobenzene hydrochloride is filtered off, washed with 2 p.c. hydrochloric acid, centrifuged and dried at 60°. The yield is 41 kilos. of dry aminoazobenzene hydrochloride. The old aniline yellow was the oxalate of the base. The free base crystallises in yellow rhombic prisms. M.p. 127·4° ; b.p. above 300°. The hydrochloride crystallises in steel-blue needles. Base slightly

[1] **Wool Scarlet R** (Sch.), **Croceine 3 B** (Sch.), and **Diamine Red NO** (C.) are no longer manufactured, according to information received by the writer from the manufacturers indicated. Since the firm Brooke, Simpson, and Spiller, Ltd., ceased to exist, some of the colouring matters made by them are now manufactured by Messrs. Claus and Co., of Manchester.

soluble in hot water, readily soluble in alcohol. Yellow solution coloured red by hydrochloric acid.

Literature.—Mène, 1861 (*see* above); Dale and Caro, E. P. 3307 of 1863; Martius und Griess, Zeitsch. f. Chem. 1866, 2, 132; Kekulé *ibid.* 2, 689; Witt and Thomas, Chem. Soc. Trans. 1883, 43, 112; Friswell and Green, *ibid.* 1885, 47, 917; and 1886, 49, 746; Städel and Bauer, Ber. 1886, 19, 1953.

Butter Yellow; Oil Yellow (W.); Dimethylaminoazobenzene, $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N(CH_3)_2$. Prepared by the action of diazobenzene chloride on dimethylaniline. Substance forms yellow leaflets of m.p. 115°; soluble in dilute hydrochloric acid with a red colour; precipitated by alkali. Soluble in strong sulphuric acid with a yellow colour, becoming red on dilution.

Literature.—Griess, Ber. 1877, 10, 528.

Chrysoïdine (most firms); **Chrysoïdine Y** (H.) (W.); **Chrysoïdine JEE** (C. J.); **Chrysoïdine Crystals;** Chrysoïdine **Small Crystals** (T. M.)

Diaminoazobenzene $C_6H_5 \cdot N_2 \cdot C_6H_3(NH_2)_2$.
$$[1] \qquad [2:4]$$

This colouring matter is prepared by mixing a solution of diazobenzene chloride with a solution of *m*-phenylenediamine. In practice a known weight of aniline is dissolved in dilute hydrochloric acid and diazotised, the solution being diluted so as to contain about 2–3 p.c. of diazo- salt. This and a dilute solution of phenylenediamine hydrochloride are run simultaneously into a sodium chloride solution, and the colouring matter is filtered off through a filter press. The press cake is then dissolved in hot dilute hydrochloric acid, the hot solution filtered, and hydrochloric acid added to the filtrate. The chrysoïdine separates in small needles, which are filtered off, centrifuged, and dried at 50°. The free base forms yellow needles; m.p. 117·5°. Slightly soluble in water, readily in alcohol; solutions orange. The commercial product is the hydrochloride $C_{12}H_{12}N_4$,HCl, which forms beautiful blackishgreen prisms with a metallic lustre. The strong solution of the salt solidifies on rapid cooling to a red jelly. Dissolves in strong sulphuric acid with a brownish-yellow colour.

Literature.—Hofmann, Ber. 1877, 10, 213; Witt, *ibid.* 350 and 654; Griess, *ibid.* 389.

Chrysoïdine R (H.) (W.) (G.) (L.); **Chrysoïdine REE** (P.); **Cerotine Orange** (C. J.); **Gold Orange for Cotton** (T. M.) (D. H.); Benzeneazo-*m*-tolylenediamine $C_6H_5 \cdot N_2 \cdot C_6H_2(CH_3)(NH_2)_2$. Prepared from aniline and *m*-tolylenediamine as in the preceding case. The free base melts at 165°–166°. The commercial product is the hydrochloride, which forms yellowish-brown lumps. Dissolves in strong sulphuric acid with a greenish-yellow colour.

Chrysoïdine R (D. H.); Tolueneazo-*m*-tolylenediamine $CH_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(CH_3)(NH_2)_2$. Prepared as above from *o*-toluidine and tolylenediamine. The commercial product the hydrochloride. It is a crystalline violet powder which gives a brown colour in strong sulphuric acid.

Meta Chrome Brown B (A.): Dinitrophenol-azo-*m*-tolylenediamine

$$OH \cdot C_6H_2(NO_2)_2N_2 \cdot C_6H_2(CH_3)(NH_2)_2.$$

Prepared from picramic acid and *m*-tolylene

¹ Chrysoïdine Crystals also contain the homologues from *o*- and *p*-toluidine.

diamine. It is a brown paste giving a dark orange-red solution in hot water. It yields a red solution with strong sulphuric acid.

Literature.—E. P. 22886 of 1899; D. R. P. 112819.

Chrome Brown P (P.); Dinitrophenolazo-*m*-aminophenol $OH \cdot C_6H_2(NO_2)_2 \cdot N_2 \cdot C_6H_3(OH) \cdot NH_2$. Prepared from picramic acid and *m*-aminophenol. Introduced in 1903.

Literature.—D. P. 169579; F. P. 336559.

Diazine Green (K.); **Janus Green B** (M.):

$$C_2H_5 \cdot N \cdot C_6H_3 < \overset{N}{\underset{N}{\big|}} > C_6H_3 \cdot N_2 \cdot C_6H_4 \cdot N(CH_3)_2.$$

$$\overset{|}{\underset{Cl \quad C_6H_5}{}}$$
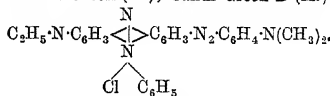
Prepared from diazotised diethylsafranine and dimethylaniline. The commercial product is a brown or dark-green powder giving an olivegreen solution with strong sulphuric acid. **Janus Green G** is a dye-stuff of analogous constitution.

Literature.—E. P. 7337 of 1897; F. P. 265438; D. R. P. 95668.

II. ACID AZO- COMPOUNDS.

A. Sulphonic Acids of Aminoazo- Compounds.

Acid Yellow (A.); **Fast Yellow** (B.) (By.); **Fast Yellow G; New Yellow L** (K.); **Yellow SS** (P.); **Fast Yellow extra** (By.). This colouring matter is a mixture of the sodium salts of mono- and di- sulphonic acids of aminoazobenzene

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH_2 \text{ and}$$
$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(HSO_3) \cdot NH_2.$$
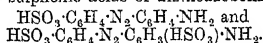
Prepared by the action of fuming sulphuric acid on aniline yellow (3–5 parts acid to one of aminoazobenzene). Solution not precipitated by alkali; colour dissolves in strong sulphuric acid with a brownish-yellow colour becoming redder on dilution. Solution gives a precipitate with barium chloride, but not with calcium chloride. The corresponding colouring matter from aminoazotoluene is somewhat more orange in shade, and is known as **Fast Yellow** (B.); **Yellow W** (By.); **Fast Yellow R** (K.).

Literature.—Grässler, E. P. 43 of 1879; A. P. 253598; D. R. P. 4186, 7094; Chem. Ind. 1879, 3, 48, 346; Griess, Ber. 1882, 15, 2187; Eger. Ber. 1889, 22, 847.

Methyl Orange; Helianthin; Orange III.; Gold Orange; *p*-Sulphobenzeneazodimethylaniline $HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N(CH_3)_2$. Prepared by the action of diazotised sulphanilic acid on dimethylaniline. Solution of colouring matter orange, and not precipitated by alkali; dilute acids produce a crystalline precipitate, the crystals having a violet reflexion (the free sulphonic acid). The substance dissolves in strong sulphuric acid with a yellow colour becoming red on dilution.

Literature.—Griess, Ber. 1877, 10, 528.

Tropæoline OO (C.); **Orange IV.** (P.); **Diphenylamine Orange; Acid Yellow D** (A.); **Orange N** (B.); **New Yellow** (By.); **Orange M** (L.); *p*-Sulphobenzeneazodiphenylamine

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH \cdot C_6H_5.$$
$$[4] \qquad [1] \qquad \underbrace{}_{[4]}$$
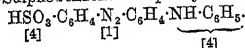
¹ For detailed information on the manufacture of sulphanilic acid and its homologues *see* Mühlhäuser, Dingl. poly. J. 1887, 264, 181 and 238; Paul, Zeitsch. angew. Chem. 1896, 9, 686.

Produced by the action of diazotised sulphanilic acid on diphenylamine dissolved in alcohol or crude carbolic acid. The product is thrown on an open filter, the paste dissolved in concentrated aqueous potassium carbonate and precipitated by adding sodium hydroxide. The colouring matter is not very readily soluble in water: the solution is yellow, and when strong deposits crystals on cooling. Substance dissolves in strong sulphuric acid with a violet colour, becoming redder and giving a greyish precipitate of the free sulphonic acid on dilution. The aqueous solution of the substance is coloured red by dilute acids.

When nitrated this colour furnishes a mono-nitro- derivative together with a mixture of mono-, di-, and tri- nitrodiphenylamine; moderate nitration yields a yellow colouring matter which is found in commerce under the names of **Citronine** (O.); **Curcumeïne** (A.); **Azoflavine 3 R** ex. conc. (T. M.); **Citronine NE** (P.). More energetic nitration of Orange IV. furnishes **Azo Acid Yellow** (A.); **Azo Yellow** (M); **Azo Yellow 3 G**, ex. conc. (T. M.); **Citronine 2 AEJ** (P.); **Azoflavine** (B.); **Indian Yellow** (By.). Both dyestuffs are ochre-yellow powders and give with strong sulphuric acid reddish-violet and magenta-red solutions respectively.

Metanil Yellow (O.), (B.), (A.), (C. J.); **Orange MN** (I.); **Tropæoline G** (C.); **Yellow M** (P.); **Metanil Yellow GR extra** (T. M.).; *m*-Sulphobenzeneazodiphenylamine

$$\text{HSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_5.$$
[3]   [1]
                         [4]
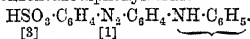
Prepared in the same manner as the preceding from *m*-diazobenzenesulphonic acid [1] and diphenylamine. Aqueous solution orange, giving no precipitate with alkalis, becoming red and precipitating with dilute acids. Dissolves in strong sulphuric acid with a dull violet colour, becoming magenta-red on dilution.

Metanil Yellow S; **Acid Yellow 2 G**, is produced by sulphonating the preceding colouring matter.

Literature.—E. P. 1226 of 1879; 4966 of 1880; Paul, Zeitsch. angew. Chem. 1896, 9, 686.

Fast Yellow N (P.); **Jaune Solide N**; **Curcumeïne**; Sulphotolueneazodiphenylamine

$$\text{HSO}_3 \cdot \text{C}_7\text{H}_6 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_5$$
[1]   [4]
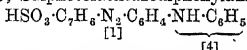
This colouring matter is homologous with the two preceding, which it resembles in its general properties.

Literature.—Roussin and Poirrier, E. P. 4491 of 1878.

Archil Substitute V; *p*-Nitrobenzeneazo-α-naphthylamine-*p*-sulphonic acid

$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_5(\text{NH}_2) \cdot \text{HSO}_3.$$
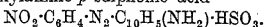
Prepared by the action of diazotised *p*-nitroaniline on naphthionic acid [2] in weakly acid solution. Solution precipitated by acids and alkalis. Strong sulphuric acid gives a magenta-red solution, becoming brownish and precipitating on dilution.

[1] *m*-Aminobenzenesulphonic acid is prepared by sulphonating nitrobenzene and reducing the *m*-nitrobenzenesulphonic acid thus formed.

[2] Naphthionic acid is manufactured on a large scale by heating α-naphthylamine with 3–4 parts of strong sulphuric acid or by heating dry naphthylamine sulphate to 180°–200°.

Literature.—Roussin and Poirrier, E. P. 4490 of 1878; D. R. P. 6715; F. P. 127221; Chem. Ind. 1879, 2, 292.

Archil Substitute 3 VN (P.); **Archil Substitute V** (A.); *p*-Nitrobenzeneazo-α-naphthylaminesulphonic acid

$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_5(\text{NH}_2) \cdot \text{SO}_3\text{H}.$$

Prepared by the action of diazotised *p*-nitroaniline on α-naphthylamine-5-sulphonic acid. Forms a brown powder giving a red solution in water or strong sulphuric acid.

Literature.—E. P. 12692 of 1887; D. R. P. 45787; F. P. 185908.

Palatine Chrome Brown W (B.); *p*-Sulpho-*o*-hydroxybenzeneazo-*m*-phenylenediamine

$$\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2)_2.$$
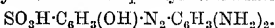
Prepared from diazotised *o*-aminophenol-*p*-sulphonic acid and *m*-phenylenediamine. A black-brown powder dissolving in hot water with an orange-brown colour, and in strong sulphuric acid to give a dark orange-brown solution.

Literature.—A. P. 628814; F. P. 284741.

Anthracyl Chrome Green (D.); Dinitrophenolazo-α-naphthylamine-4-sulphonic acid

$$\text{OH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_5(\text{SO}_3\text{H}) \cdot \text{NH}_2.$$
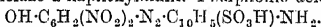
Prepared by the action of diazotised picramic acid on naphthionic acid. Solution in water is reddish-brown, and in strong sulphuric acid bluish fiery red.

Literature.—D. P. 142153.

Alkali Brown (D.); **Benzo Brown 5 R** (By.); **Alkali Brown R** (L. P.); **Cotton Brown R** (B.); **Terra Cotta** (G.); Primulineazo-*m*-phenylenediamine P[1] ·N_2·C_6H_3(NH_2)_2. Prepared from diazotised primuline or dehydrothio-*p*-toluidinesulphonic acid on *m*-phenylenediamine. Solution brownish-red, precipitated by acids or alkalis. Gives a bluish-violet solution with strong sulphuric acid.

Apollo Red (G.); **Archil Substitute extra** (C.); *p*-Nitrobenzeneazo-α-naphthylaminedisulphonic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_4(\text{NH}_2)_2$. Prepared from diazotised *p*-nitroaniline and α-naphthylamine-4: 6- or 4: 7-disulphonic acid. Gives a brownish-red solution in water and a magenta-red in strong sulphuric acid.

Literature.—E. P. 9468 of 1887; A. P. 376392; F. P. 184638.

Brilliant Archil C (C.); **Brilliant Wool Scarlet** (K); Azimide of *p*-nitrobenzeneazo-1 : 8-naphthylenediaminedisulphonic acid

$$\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_2 \underset{\text{N}}{\overset{\text{N}}{\text{N}}}$$
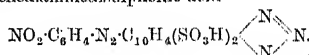
Prepared by the action of nitrous acid on the product from diazotised *p*-nitroaniline and 1 : 8-naphthylenediamine-3 : 6-disulphonic acid. A brownish-red powder dissolving in water with a red, and in strong sulphuric acid with a blue, solution.

Literature.—E. P. 24714 of 1893; D. R. P. 77425; F. P. 234837.

Wool Violet S (B.); Dinitrobenzeneazodiethylmetanilic acid

$$(\text{NO}_2)_2\text{C}_6\text{H}_3 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{SO}_3\text{H}) \cdot \text{N}(\text{C}_2\text{H}_5)_2.$$
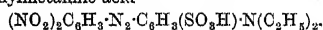
Prepared from diazotised 2 : 4-dinitroaniline and diethylmetanilic acid. A black powder

[1] P = the residue of primuline.

giving a reddish-violet solution in water and a scarlet-red in strong sulphuric acid.

Literature.—E. P. 6197 of 1894; D. R. P. 86071; F. P. 239096; A. P. 525656.

Salmon Red (A.); Methylbenzenylamino-thioxylenolazo-β-naphthylamine-3 : 6-disulphonic acid
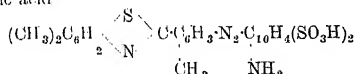
$$(CH_3)_2C_6H \underset{2}{\overset{S}{\underset{N}{\diagdown}}} C \cdot C_6H_3 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2$$
$$\underset{CH_3}{\quad} \underset{NH_2}{\quad}$$

Prepared from diazotised dehydrothio-*m*-xylidine and β-naphthylamino-3 : 6-disulphonic acid R. Aqueous solution is orange red. Gives violet solution in strong sulphuric acid.

Literature.—Paul, Zeitsch. angew. Chem. 1896, 9, 680.

Brilliant Yellow S (B.) (T. M.); **Yellow WR** (I.); **Curcumine** (G.); *p*-Sulphobenzeneazodiphenylaminesulphonic acid. Prepared by sulphonating orange IV. Solution in water is yellow and in strong sulphuric acid bluish-red.

Literature.—D. R. P. 21903.

Lanacyl Violet B (C.); Disulphohydroxy-naphthaleneazoethyl-a-naphthylamine

$$(HSO_3)_2C_{10}H_4(OH) \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot C_2H_5.$$

Prepared from diazotised 1 : 8-aminonaphthol-3 : 6-disulphonic acid and ethyl-α-naphthylamine. Solution in water is reddish-violet, and in strong sulphuric acid is greenish-blue.

Literature.—E. P. 12556 of 1896; D. R. P. 94288; F. P. 257136.

B. Carboxylic Acids of Aminoazo- Compounds.

Yellow fast-to-soap (P.); **Orange MG** (P.); *m*-Carboxybenzeneazodiphenylamine

$$CO_2H \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NH \cdot C_6H_5.$$
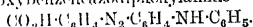
Prepared by the action of *m*-diazobenzoic acid on diphenylamine. Used in wool-dyeing and especially calico-printing; the shades are very fast to soap. A brown paste, difficultly soluble in water. Solution becomes reddish-violet with acids. Dissolves with a violet colour in strong sulphuric acid, becoming red on dilution.

Literature.—E. P. 4621 of 1883; D. R. P. 29991; F. P. 157755; A. P. 297852.

C. Hydroxyazo- Compounds.

Sudan Brown (A.); **Pigment Brown** (B.); α-Naphthaleneazo-α-naphthol
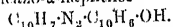
$$C_{10}H_7 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared by the action of diazotised α-naphthylamine on α-naphthol in alkaline solution.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799; Frankland, Trans. Chem. Soc. 1880, 37, 752.

Sudan G (A.) (F.) (Ib.) (W.); **Carminaph J** (D. H.); **Cerasine Orange G** (C.); **Cerotine Yellow R** (C. J.); **Chrysoïn insoluble** (P.); Benzeneazoresorcinol $C_6H_5 \cdot N_2 \cdot C_6H_3(OH)_2$. Prepared by the action of diazobenzene chloride on resorcinol in alkaline solution. Solution of colouring matter yellow, giving a brown precipitate with acids. Dissolves in strong sulphuric acid with a yellowish-brown colour.

Literature.—Baeyer and Jäger, Ber. 1875, 8, 151; Typke, *ibid.* 1877, 10, 1576; Wallach, *ibid.* 1881, 14, 24; Wallach and Fischer, *ibid.* 1882, 15, 2814; Meyer and Kreis, *ibid.* 1883, 16, 1329; Liebermann and Kostanecki, *ibid* 1884, 17, 880; Heumann and Oeconomides,

ibid. 1887, 20, 904; Will and Pukall, *ibid.* 1120; Pukall, *ibid.* 1147; Fischer and Wimmer, *ibid.* 1578; Will, *ibid.* 1888, 21, 604; Kostanecki, *ibid.* 3119.

Sudan I (A.) (F.) (Ib.) (K.) (W.); **Carminaph** (D. H.); **Cerotine Orange G** (C. J.); Benzeneazo-β-naphthol $C_6H_5 \cdot N_2 \cdot C_{10}H_6 \cdot OH$. Prepared from diazobenzene chloride and β-naphthol.** A brick-red powder insoluble in water. Used for colouring oils, &c.

Literature.—Liebermann, Ber. 1883, 16, 2860; Denare, Gazz. chim. ital. 1885, 15, 406; Zincke and Bindewald, Ber. 1884, 17, 3031; Zincke and Rathgen, *ibid.* 1886, 19, 2484; Fischer and Wimmer, *ibid.* 1887, 20, 1579; Weinberg, *ibid.* 3172; Jacobson, *ibid.* 1888, 21, 415; Meldola and East, Trans. Chem. Soc. 1888, 53, 460; Meldola and Morgan, *ibid.* 1889, 55, 603; Goldschmidt and Rosell, Ber. 1890, 23, 496; Goldschmidt and Brubacher, *ibid.* 1891, 24, 2306; McPherson, Ber. 1895, 28, 2418; Farmer and Hantzsch, 1899, 32, 3100; Möhlau and Strohbach, *ibid.* 1900, 33, 805; Goldschmidt and Keppeler, *ibid.* 894; Möhlau and Kegel, *ibid.* 2873; Betti, Gazz. chim. ital. 1900, 30, ii. 164.

Sudan II (A.) (K.); **Red B** (B.) (Fi.); **Cerotine Scarlet G** (C. J.); Xyleneazo-β-naphthol

$$C_6H_3(CH_3)_2 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared from diazotised xylidine and β-naphthol.

Carminaph Garnet (D. H.); **Cerotine Scarlet 2 R** (C. J.); α-Naphthaleneazo-β-naphthol

$$C_{10}H_7 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared from diazotised α-naphthylamine and β-naphthol. An insoluble paste used in printing. (*See* also **Naphthylamine Bordeaux**, p. 363.)

Azophosphine GO (M.); Chloride of *m*-trimethylaminobenzeneazoresorcinol

$$ClN(CH_3)_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH)_2.$$

Prepared from diazotised *m*-aminophenyltrimethylammonium chloride and resorcinol. Solution in water is yellowish-red, and in strong sulphuric acid brownish-red.

Literature.—E. P. 14494 of 1895; D. R. P. 87257; F. P. 249227.

New Phosphine G (C.); ω-Dimethylamino-tolueneazoresorcinol,

$$N(CH_3)_2 \cdot CH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH)_2.$$
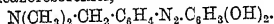
Prepared from diazotised *p*-aminobenzyldimethylamine and resorcinol. Gives a yellowish-brown solution in water and strong sulphuric acid.

Literature.—E. P. 22572 of 1892; D. R. P. 70678; F. P. 225968; A. P. 515100.

Tannin Orange R (C.); ω-Dimethylamino-tolueneazo-β-naphthol

$$N(CH_3)_2 \cdot CH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$
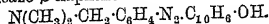
Prepared from diazotised *p*-aminobenzyldimethylamine and β-naphthol. A brown powder or a 50 p.c. paste. Sparingly soluble in water, with a brown colour. Gives a yellowish-brown solution in strong sulphuric acid.

Literature.—As for the preceding colour.

Azochromine (G.); Tetrahydroxyazobenzene $OH \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(OH)_3$. Prepared from diazotised *p*-aminophenol and pyrogallol. Commercial product as a 30 p.c. paste, giving a dark-yellow solution in boiling water. With strong sulphuric acid it gives a brown solution.

Literature.—E. P. 11902 of 1893; D. R. P. 81109; F. P. 230937; A. P. 548460.

Diazine Black (K.); **Janus Grey B** (M.); Safranineazophenol. Prepared from one of the varieties of safranine and phenol. Its solution in water is blackish-green blue, and in strong sulphuric acid green.

- *Literature.*—Mon. Sci. 1886, (iii.) 16, 984.

Indoine Blue R (B.) (G.); **Janus Blue** (M.); **Naphthindone** (C.); **Bengaline** (K.); **Vae Blue** (H.); **Fast Cotton Blue R** (O.); **Indole Blue R** (A.); **Diazine Blue** (K.); **Madras Blue P** (P.); Safranineazo-β-naphthol. Prepared from various safranines and β-naphthol. It gives a violet solution in water, and a greenish-brown in strong sulphuric acid.

Literature.—E. P. 4543 of 1891, 18769 of 1893, 3488 of 1895, 23985 of 1898; D. R. P. 61692, 85690, 85932, 91721, 92015, 105433, 108497; F. P. 212276, 245239, 250239, 233013, 285360; A. P. 524251, 524254; Walter, Aus der Praxis der Anilinfarbenfabrikation, 1903, 306 (where the preparation is described in detail).

D. Sulphonic Acids of Hydroxyazo- Compounds.

1. MONOSULPHONIC ACIDS.

Tropæoline O (C.); **Resorcin Yellow** (A.); **Chrysoïn** (B.); **Chryseoline**; **Gold Yellow** (By.); **Yellow T** (I.); **Acme Yellow** (L.); *p*-Sulpho-benzeneazoresorcinol $HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH)_2$. Produced by the action of diazotised sulphanilic acid on resorcinol in alkaline solution. Solution of colouring matter orange; substance dissolves in strong sulphuric acid with a yellow colour.

Literature.—Griess, Ber. 1878, 11, 2195; Witt, Trans. Chem. Soc. 1879, 35, 183.

Orange II (most firms); **Tropæoline OOO, No. 2**; **Betanaphthol Orange**; **Mandarin G Extra** (A.); **Gold Orange** (By.); **Orange Extra** (C.); **Orange A** (L.); **Gold Orange extra conc.** (T.M.); *p*-Sulphobenzeneazo-β-naphthol

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$
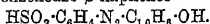
Prepared from diazotised sulphanilic acid and β-naphthol. Solution orange, becoming red on addition of sodium hydroxide. Solution in strong sulphuric acid red, becoming orange on dilution.

Literature.—Hofmann, Ber. 1877, 10, 1378; Griess, *ibid.* 1878, 11, 2198; Witt, *ibid.* 1879, 12, 259; Miller, *ibid.* 1880, 13, 268; Witt, Chem. Zeit. 1880, 4, 437; Mühlhäuser, Dingl. Poly. J. 1887, 264, 181, 238; Paul, Zeitsch. angew. Chem. 1896, 9, 686 (the last two papers give details of the manufacture).

Orange R (I.); **Orange T** (K.); **Kermesin Orange** (L.); **Mandarin GR** (A.); Sulpho-*o*-tolueneazo-β-naphthol

$$HSO_3 \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta).$$
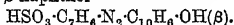
Homologous with the preceding, the diazotised sulphonic acid of *o*-toluidine being used instead of sulphanilic acid.

Orange 2 R (I.); **Orange R** (B.); Sulphoxylene-azo - β - naphthol $HSO_3 \cdot C_8H_5 \cdot N_2 \cdot C_{10}H_6 \cdot OH(\beta)$. Prepared in the same manner as the preceding from the sulphonic acid of commercial xylidine and β-naphthol. Aqueous solution gives a reddish-brown precipitate with dilute acids. Dissolves with a red colour in strong sulphuric acid, giving a brown precipitate on dilution.

Literature.—The manufacture of the two last colouring matters is described in the paper by Mühlhäuser already referred to.

Azofuchsine B (By); Tolueneazo-1 : 8-dihy-droxynaphthalenesulphonic acid

$$CH_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_4(OH)_2 \cdot SO_3H.$$
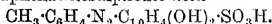
Prepared by the action of diazotised commercial toluidine on 1 : 8-dihydroxynaphthalene-4-sulphonic acid. Solution in water is bluish-red, and in strong sulphuric acid violet.

Literature.—E. P. 18517 of 1889; D. R. P. 54116; F. P. 203744; A. P. 466841, 468142.

Ponceau 4 GB (A.) (Lev.); **Croceïne Orange** (By.) (C.); **Brilliant Orange G** (M.) (C.J.); **Orange GRX** (B.); Benzeneazo-β-naphtholsulphonic acid

$$C_6H_5 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH(\beta).$$

Prepared by the action of diazobenzene chloride on β-naphthol-6-sulphonic acid (Schäffer's acid) in alkaline solution. Solutions in water or strong sulphuric acid are orange-yellow.

Literature.—Griess, Ber. 1878, 11, 2197.

Orange GT (By.); **Orange RN** (C.); **Orange O** (M.); Tolueneazo-β-naphthol-sulphonic acid $C_7H_7 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH(\beta)$. Prepared by diazotising commercial toluidine and combining with Schäffer's β-naphtholmonosulphonic acid in alkaline solution. Orange aqueous solution gives an oily precipitate with acids. Dissolves in strong sulphuric acid with a magenta-red colour, giving an oily deposit on dilution.

Scarlet GR (A.); **Scarlet R** (By.); **Brilliant Orange R** (M.) (C. J.); **Orange L** (Lev.) (P.). Homologous with the last; prepared from diazotised xylidine and Schäffer's acid. Dissolves in strong sulphuric acid with a red colour, becoming brown and precipitating on dilution.

Literature.—Levinstein, Ber. 1880, 13, 586.

Azococeine 2 R (A.); **Double Scarlet R** (Lev.); Xyleneazo-α-naphtholsulphonic acid

$$(CH_3)_2C_6H_3 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH(\alpha).$$
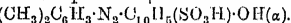
Prepared by the action of diazoxylene chloride (commercial xylidine diazotised) on α-naphthol-4-sulphonic acid in alkaline solution. Aqueous solution not precipitated by alkalis; when hot and concentrated deposits bronzy crystals on cooling. Dissolves in strong sulphuric acid with a reddish-violet colour, becoming brown and precipitating free acid on dilution.

Literature.—E. P. 2237 of 1883; D. R. P. 26012.

Azo Grenadine L (By.); Acetylaminoben-zeneazo-α-naphthol-4-sulphonic acid

$$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$$
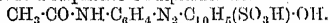
Prepared from diazotised *p*-aminoacetanilide and α-naphthol-4-sulphonic acid. Magenta-red aqueous solution becomes orange-red with sodium hydroxide. Solution in strong sulphuric acid is red.

Azoeosine (By.) (Lev.); **Azoeosine G** (K.); Anisoleazo-α-naphthol-4-sulphonic acid

$$CH_3 \cdot O \cdot C_6H_3 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$$
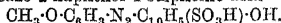
Prepared from diazotised *o*-anisidine and α-naphthol-4-sulphonic acid. Gives a red solution in water and a carmine-red in strong sulphuric acid.

Literature.—E. P. 2237 of 1883.

Benzoyl Pink; **Rose de Benzoyl** (P.); Benz-oylaminoditolylazo-α-naphthol-4-sulphonic acid

$$C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH$$
$$\hspace{2cm} | \hspace{1cm} | \hspace{1.5cm} |$$
$$\hspace{2cm} CH_3 \hspace{0.3cm} CH_3 \hspace{1cm} SO_3H$$
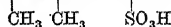
Prepared from diazotised monobenzoyl-*o*-tolui-dine and α-naphthol-4-sulphonic acid. A brick-

red paste, giving a cherry-red solution in water, and a bluish-red solution in strong sulphuric acid.

Literature.—D. R. P. 60332.

Fast Red BT (By.) (Lev.) (D.H.); α-Naphthaleneazo-β-naphthol-6-sulphonic acid

$$C_{10}H_7 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$$
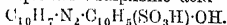
Prepared from diazotised α-naphthylamine and β-naphthol-6-sulphonic acid (Schäffer). Gives a red solution in water and a violet in strong sulphuric acid.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799.

Fast Brown N (By.); **Acid Brown O** (M.); **Naphthalamine Brown**; *p*-Sulphonaphthaleneazo-α-naphthol $HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$ Prepared by the action of diazotised α-naphthylamine-4-sulphonic acid (naphthionic acid) on α-naphthol in alkaline solution. Colouring matter gives a reddish-brown solution, not changed by acids or alkalis. Dissolves in strong sulphuric acid with a reddish-violet colour.

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799.

Fast Brown 3 B (A.); Sulphonaphthalene-2-azo-α-naphthol $HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$ Prepared by the action of diazotised β-naphthylamine-6-sulphonic acid on α-naphthol in alkaline solution.

Aqueous solution brownish-red, becoming violet with dilute acids and red with alkalis. Solution in strong sulphuric acid blue, giving a reddish-violet precipitate on dilution.

Literature.—E. P. 3724 of 1882; D. R. P. 22547; F. P. 150503; A. P. 332829.

Chrome Fast Cyanine G (I.), introduced into commerce in 1907, is prepared by the action of diazotised 1-amino-2-naphtholsulphonic acid on α-naphthol.

Eriochrome Blue Black B (G.); Sulphonaphtholazo-α-naphthol
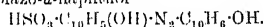
$$HSO_3 \cdot C_{10}H_5(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared by the action of diazotised 1-amino-β-naphthol-4-sulphonic acid on α-naphthol.[1] The blackish-violet aqueous solution on addition of hydrochloric acid becomes first reddish-brown, and then gives a brownish-black precipitate. With sodium hydroxide the solution becomes first blue and, on adding excess, finally red. The solution in strong sulphuric acid is blue, giving a violet-black precipitate on dilution.

Literature.—E. P. 15025 of 1904; D. R. P. 181326; F. P. 350055; Ital. P. 73530; Aust. P. 30630.

Eriochrome Black T (G.); Nitrosulphonaphtholazo-α-naphthol

$$NO_2 \cdot C_{10}H_4(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$
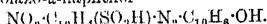
Prepared by the action of diazotised 8-nitroamino-β-naphthol-4-sulphonic acid on α-naphthol. The reddish-brown aqueous solution gives a violet-brown precipitate with hydro-

[1] In the constitutional formula of this colouring matter, kindly communicated along with other information to the writer by the manufacturers, the azo- group is shown attached to the 2- position of the α-naphthol, although the 4- position is unoccupied. The combination is probably effected in presence of very concentrated alkali hydroxide. Other examples of this ortho- combination are known, both in the benzene and naphthalene series. (Compare Michel and Grandmougin, Ber. 1893, 26, 2353; Bamberger, *ibid.* 1900, 33, 3188; Bamberger and Meimberg, *ibid.* 1895, 28, 1889; Bamberger, *ibid.* 848; D. P. 14443.)

Vol. I.—T.

chloric acid, and, with sodium hydroxide, becomes first deep-blue and then red. The solution in strong sulphuric acid is blackish-blue, giving a brown precipitate on dilution.

Literature.—E. P. 15982 of 1904; D. R. P. 169683; F. P. 350071; Ital. P. 73531; Aust. P. 27191.

Brilliant Double Scarlet G (A.) (Lev.) (K.); **Scarlet for silk** (M.); **Ponceau for silk** (P.).— Prepared from β-naphthylamine-6-sulphonic acid and β-naphthol. Aqueous solution gives brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour, giving a brown precipitate on dilution.

Literature as under **Fast Red B.**

Fast Red; **Fast Red A** (B.) (C. J.) (Lev.); **Roccelline** (D. H.); **Rauracienne**; **Rubidine**; Sulphonaphthaleneazo-β-naphthol

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$
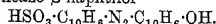
Prepared by the action of diazotised naphthionic acid on β-naphthol in alkaline solution. Substance dissolves in hot water with a reddish-brown colour; concentrated solution when rapidly cooled solidifying to a brown gelatinous mass. Soluble in strong sulphuric acid with a violet colour, becoming brown and giving a precipitate of the free acid on dilution. The corresponding colouring matter from α-naphthylamine-5-sulphonic acid is called **Brilliant Fast Red G** (B.).

Literature.—E. P. 786 of 1878; D. R. P. 5411; F. P. 123148; A. P. 204799; Griess, Ber. 1878, 11, 2199; 1879, 12, 1364.

Acid Ponceau (D. H.); **Fast Acid Scarlet**; **Ponceau S for silk** (I.); **Ponceau G for silk** (K.); Sulpho-β-naphthaleneazo-β-naphthol

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$
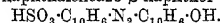
Prepared by sulphonating β-naphthylamine, diazotising the mixed isomeric sulphonic acids, and combining with β-naphthol in alkaline solution. Aqueous solution gives a brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour, becoming brown and precipitating on dilution.

Lithol Red B (B.); Sulphonaphthaleneazo-β-naphthol $HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$ Prepared by the action of diazotised β-naphthylamine-1-sulphonic acid on β-naphthol. The commercial product is a paste which is only very sparingly soluble even in hot water. It is used exclusively in the manufacture of lakes.

Literature.—E. P. 25511 of 1899; D. R. P. 112833; F. P. 297330; A. P. 650757.

Clayton Cloth Red (Cl. Co.); **Stanley Red** (Cl. Co.); Sulphobenzenylaminothiocresolazo-β-naphthol

$$CH_3 \cdot C_6H_3 \left\langle \begin{matrix} N \\ S \end{matrix} \right\rangle C \cdot C_6H_4(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared by the action of diazotised dehydro-*p*-toluidinesulphonic acid on β-naphthol. The commercial product is the ammonium salt. Forms a reddish-brown solution in water, and a violet-red with strong sulphuric acid.

Literature.—E. P. 18901 of 1889; D. R. P. 51331.

Acid Alizarine Black R (M.); Nitrosulphophenolazo-β-naphthol

$$OH \cdot C_6H_2(NO_2)(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared from diazotised 6-nitro-2-aminophenol-4-sulphonic acid and β-naphthol. Aqueous

2 B

solution is brownish-violet, and solution in strong sulphuric acid is reddish-violet.

Literature.—E. P. 2772 of 1900; D. R. P. 143892; A. P. 667935.

Anthracene Chrome Black (C.); Sulphonaphtholazo-β-naphthol

$$HSO_3 \cdot C_{10}H_5(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$

Prepared by the action of diazotised 3-amino-β-naphthol-7-sulphonic acid (R.) on β-naphthol. Aqueous solution is red; hydrochloric acid gives a reddish-violet precipitate, and sodium hydroxide turns it bluish-violet. Solution in strong sulphuric acid is bluish-green, giving a reddish-violet precipitate on dilution.

Literature.—E. P. 28107 of 1897; D. R. P. 109932; F. P. 272620, 272621.

Palatine Chrome Blue (B.); **Eriochrome Blue Black R** (G.). Isomeric with the preceding. Prepared from diazotised 1-amino-β-naphthol-4-sulphonic acid and β-naphthol. Blue aqueous solution gives yellowish-brown precipitate with hydrochloric acid, and turns first blue and then red with sodium hydroxide. Solution in strong sulphuric acid is dark blue, giving a blackish-brown precipitate on dilution.

Literature.—E. P. 15025 of 1904; F. P. 350055; Ital. P. 73530; Aust. P. 30630.

Salicin Black U (K.) is the zinc sodium salt of the above, and is prepared by diazotising 1-amino-β-naphthol-4-sulphonic acid with zinc nitrite and combining the diazo-compound with β-naphthol in concentrated alkaline solution.

Literature.—E. P. 23034 of 1905; D. R. P. 175593, 195228; F. P. 353786; A. P. 807422.

Eriochrome Black A (G.); Nitrosulphonaphtholazo-β-naphthol

$$NO_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$$
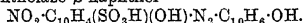
Prepared from diazotised 8-nitro-1-amino-β-naphthol-4-sulphonic acid and β-naphthol. Dark-blue aqueous solution gives a reddish-brown precipitate with hydrochloric acid, and becomes cherry-red with sodium hydroxide. Solution in strong sulphuric acid is dark-violet blue, giving a brown precipitate on dilution.

Literature.—E. P. 15982 of 1904; D. R. P. 169683; F. P. 350071; A. P. 790363; Ital. P. 73531; Aust. P. 27191.

Diamond Black PV (By.); Sulphophenolazo-1 : 5-dihydroxynaphthalene

$$OH \cdot C_6H_3(SO_3H) \cdot N_2 \cdot C_{10}H_5(OH)_2.$$
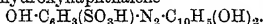
Prepared from diazotised *o*-aminophenolsulphonic acid and 1 : 5-dihydroxynaphthalene. Bluish-red aqueous solution gives a dark red precipitate with hydrochloric acid. Solution in strong sulphuric acid is blackish-green, giving a reddish precipitate on dilution.

Literature.—E. P. 18139 of 1902.

Roxamine (D. H.); Sulphonaphthaleneazo-2 : 7-dihydroxynaphthalene

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(OH)_2.$$
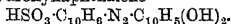
Prepared by the action of diazotised naphthionic acid on 2 : 7-dihydroxynaphthalene. Aqueous solution is scarlet. Dissolves in strong sulphuric acid with a violet colour.

Azo Acid Blue 4 R (By.). Is probably prepared by the action of diazotised *p*-nitroaniline on 1 : 8-dihydroxynaphthalene-4-sulphonic acid and subsequently reducing the nitro- group. It gives a blue-violet solution in water and a reddish-violet in strong sulphuric acid.

Literature.—Chem. Ind. 1896, 19, 549.

Milling Yellow (Lev.) (D.); **Chrome Yellow D** (By.); **Anthracene Yellow BN** (U.⁂; **Mordant Yellow O** (B.) (M.); **Chrome Fast Yellow** (A.); **Salicin Yellow D** (K.); Sulphonaphthaleneazosalicylic acid

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$
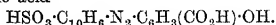
Prepared by the action of diazotised β-naphthylamine-5-(or 6)-sulphonic acid on salicylic acid. Solution in water is yellow, and in strong sulphuric acid yellowish-red.

Oriol Yellow (G.); **Cotton Yellow R** (B.); **Alkali Yellow** (D.); Primulineazosalicylic acid P ¹·N₂·C₆H₃(CO₂H)·OH. Prepared by the action of diazotised primuline on salicylic acid. Gives an orange-yellow solution in water, and a scarlet-red with strong sulphuric acid.

Literature.—D. R. P. 48465; F. P. 192628; A. P. 398990.

Eriochrome Phosphine R (G.); Nitrosulphobenzeneazosalicylic acid

$$NO_2 \cdot C_6H_3(SO_3H) \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$
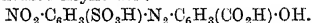
Prepared by the action of diazotised *p*-nitroaniline-*o*-sulphonic acid on salicylic acid. Yellowish-orange aqueous solution becomes pale orange with hydrochloric acid, and blue-red with sodium hydroxide. Solution in strong sulphuric acid is yellowish orange giving a pale-yellow precipitate on dilution.

Literature.—D. R. P. appl. A 17781 of 1909.

Eriochrome Red B (G.); Sulphonaphtholazophenylmethylpyrazolone

$$HSO_3 \cdot C_{10}H_5(OH) \cdot N_2 \cdot C \begin{cases} C(CH_3) : N \\ | \\ C(OH){-}N \cdot C_6H_5. \end{cases}$$
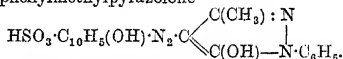
Prepared by the action of diazotised 1-amino-β-naphthol-4-sulphonic acid on phenylmethylpyrazolone. Yellowish-red aqueous solution gives a bright scarlet-red precipitate with hydrochloric acid, and becomes orange-yellow with sodium hydroxide. Solution in strong sulphuric acid is magenta-red, giving a scarlet-red precipitate on dilution.

Literature.—E. P. 17274 of 1904; D. R. P. 165743; F. P. 350161; A. P. 808919.

Dianil Yellow R (M.). Prepared by the action of diazotised primuline (sulphonic acid) on 1-phenyl-3-methylpyrazolone. The orange-yellow aqueous solution gives an orange-yellow precipitate with hydrochloric acid and a reddish-yellow one with sodium hydroxide. Solution in strong sulphuric acid is dark orange, giving an orange-yellow precipitate on dilution.

Literature.—E. P. 10127 of 1897; D. R. P. 117575.

Dianil Yellow 3 G (M.). Prepared from diazotised dehydrothio-*p*-toluidinesulphonic acid and ethyl acetoacetate. Greenish-yellow aqueous solution gives a yellow precipitate with hydrochloric acid, and becomes orange with sodium hydroxide. Solution in strong sulphuric acid is brownish-yellow, giving a yellow precipitate on dilution.

Literature.—E. P. 17328 of 1897; D. R. P. 98761; F. P. 256647, 269001; A. P. 66256.

2. Disulphonic Acids.

Phenoflavine (O.); *m*-Sulphobenzeneazoaminophenolsulphonic acid.

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(SO_3H)(NH_2) \cdot OH.$$
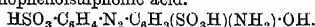
¹ P = residue of primuline.

Prepared by the action of diazotised metanilic acid on 3-aminophenol-5-sulphonic acid (III.). Gives a yellow solution in water or strong sulphuric acid.

Literature.—D. R. P. 71229.

Chrome Brown RR (G.); Disulphophenolazopyrogallol

$$OH \cdot C_6H_2(SO_3H)_2 \cdot N_2 \cdot C_6H_2(OH)_3.$$
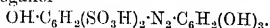
Prepared by the action of diazotised *p*-aminophenol-2 : 6-disulphonic acid on pyrogallol. Solution in water is yellow, and in strong sulphuric acid brown.

Literature.—E. P. 11902 of 1893; D. R. P. 81109; F. P. 230937; A. P. 548460.

Orange G (A.) (M.) (B.) (P.) (C. J.); **Orange GG** (C.); Benzeneazo-β-naphtholdisulphonic acid $C_6H_5 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH(\beta)$. Produced by the action of diazobenzene chloride on β-naphthol-6 : 8-disulphonic acid (G-salt) in alkaline solution. Solution not precipitated by alkali; dissolves in strong sulphuric acid with an orange colour, undergoing no change on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811.

Crystal Scarlet 6 R (C.) (M.); **Crystal Ponceau** (A.) (K.)(B.); α-Naphthaleneazo-β-naphthol-6 : 8-disulphonic acid (G-acid). Produced by the action of diazotised α-naphthylamine upon β-naphthol-6 : 8-disulphonic acid in alkaline solution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; A. P. 332528.

Ponceau 2 G (A.) (B.) (M.) (C.); **Orange R** (H.). Isomeric with Orange G. Prepared by the action of diazobenzene chloride upon β-naphthol-3 : 6-disulphonic acid (R-salt). Properties similar to those of the preceding compound; colour slightly redder in shade.

Literature as for Orange G.

Azocoralline (D.); *p*-Acetylaminobenzeneazo-β-naphthol-3 : 6-disulphonic acid
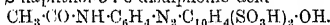
$$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on β-naphthol-3 : 6-disulphonic acid (R-salt). Solution in water is orange-red, and in strong sulphuric acid yellowish-red.

Literature.—Nietzki, Ber. 1884, 17, 344.

Ponceau R, 2 R, G and **GR** [1] (A.) (B.) (M.) (Lev.) (H.) (C.) (C. J.); **Brilliant Ponceau R** (T. M.); **Xylidine Scarlet**; **Xylidine Red**; Xyleneazo-β-naphthol-3 : 6-disulphonic acid

$$C_8H_9 \cdot N_2 \cdot C_{10}H_4(HSO_3)_2 \cdot OH(\beta).$$
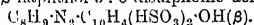
Produced by the action of diazotised xylidine (chiefly meta-) on β-naphthol-3 : 6-disulphonic acid (R-salt). Properties similar to those of Orange G. Colour a distinct scarlet; aqueous solution not precipitated by alkali; an amorphous precipitate by calcium or barium chloride. Soluble with a red colour in strong sulphuric acid, becoming brown and precipitating on dilution.

Literature.—E. P. 1715 of 1878; D.R.P. 3229; F. P. 124811; A. P. 210233.

Ponceau 3 R (A.) (B.) (M.) (C. J.) (K.); **Ponceau 4 R** [2] (A.); **Cumidine Red** (M.); Cumeneazo-β-naphthol-3 : 6-disulphonic acid

$$C_9H_{11} \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH(\beta).$$
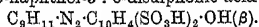
[1] **G** and **GR** are made from crude xylidine and crude R-salt, **R** from crude xylidine and **2 R** from *m*-xylidine and pure R-salt.

[2] **3 R** is made from crude cumidine and **4 R** from pure ψ-cumidine.

Produced by the action of diazocumene chloride (from ψ-cumidine) on R-salt. Properties as above; colour of a redder shade than the last.

Literature.—*See* above.

Ponceau 3 R (M.); Dimethylethylbenzeneazo-β-naphthol-3 : 6-disulphonic acid

$$C_2H_5 \cdot C_6H_2(CH_3)_2 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH(\beta).$$
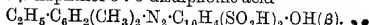
Prepared by the action of diazotised ethylxylidine on R-salt.

Literature.—*See* above.

Bordeaux B (H.) (A.) (M.); **Fast Red B** (B.); **Bordeaux BL** (C.); **Bordeaux R extra** (M.); **Cerasine** (P.); **Archilline 2 B** (Lev.); α-Naphthaleneazo-β-naphthol-3 : 6-disulphonic acid

$$C_{10}H_7 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$
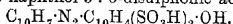
Prepared from diazotised a-naphthylamine and R-salt. Solution in water is magenta-red, and in strong sulphuric acid blue becoming magenta-red on dilution.

Literature.—E. P. 1715 of 1878; D. R. P. 3229; F. P. 124811; A. P. 251164.

Sorbine Red (B.); **Azogrenadine S** (By.); **Lanafuchsine SB** (C.); *p*-Acetylaminobenzeneazo-a-naphthol-3 : 6-disulphonic acid
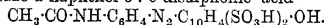
$$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$

Prepared by the action of diazotised acetyl-*p*-phenylenediamine on α-naphthol-3 : 6-disulphonic acid. Aqueous solution is currant-red, and, in strong sulphuric acid fiery red. **Lanafuchsine SG** is a closely related dyestuff.

Palatine Scarlet (B.); **Cochineal Scarlet PS** (By.); *m*-Xyleneazo-α-naphthol-3 : 6-disulphonic acid $C_8H_9 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$ Prepared from diazotised *m*-xylidine and α-naphthol-3 : 6-disulphonic acid. Solution in water is scarlet-red and in strong sulphuric acid bluish-red. Closely related dyestuffs are **Palatine Scarlet 3 R** and **4 R** (B.); **Brilliant Cochineal 2 R** and **4 R** (C.).

XL Carmoïsine 6 B (H.).; *m*-Xyleneazodihydroxynaphthalene-3 : 6-disulphonic acid $C_8H_9 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2(OH)_2$. Prepared by the action of diazotised *m*-xylidine on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid (chromatrope acid).

Eosamine B (A.); Methoxytolueneazo-α-naphthol-3 : 6-disulphonic acid

$$CH_3 \cdot O \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$
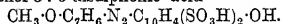
Prepared from diazotised *m*-amino-*p*-cresol methyl ether and α-naphthol-3 : 6-disulphonic acid. Solution in water is bluish-red, and in strong sulphuric acid violet-blue.

Literature.—Chem. Ind. 1896, 19, 8.

Palatine Red (B.); **Naphthorubin** (By.); α-Naphthaleneazo-α-naphthol-3 : 6-disulphonic acid $C_{10}H_7 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$ Prepared from diazotised α-naphthylamine and α-naphthol-3 : 6-disulphonic acid. Bluish-red solution in water, and blue in strong sulphuric acid. A similar colouring matter is **Azo Red A** (C.).

Literature.—E. P. 15716 of 1885; D. R. P. 38281.

Direct Rose G (K. S.):

$$CH_3 \cdot C_6H_3 \underset{N}{\overset{S}{\diagup\diagdown}} C \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$
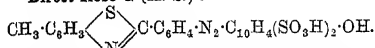
Prepared from diazotised dehydrothio-*p*-toluidine and α-naphthol-3 : 8-disulphonic acid (ε-acid). Cherry-red aqueous solution gives a scarlet-red precipitate with hydrochloric acid, and a bluish-red one with sodium hydroxide.

Solution in strong sulphuric acid is dark-bluish red, giving a scarlet-red precipitate on dilution.

Erika B (A.); Methylbenzenylaminothioxylenolazo-α-naphthol-3 : 6-disulphonic acid
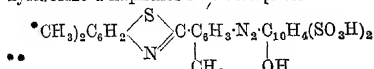
$$CH_3)_2C_6H_2\big\langle \substack{S \\ N} \big\rangle C\cdot C_6H_3\cdot N_2\cdot C_{10}H_4(SO_3H)_2$$
$$\mspace CH_3 \mspace OH$$

Prepared from diazotised dehydrothio-*m*-xylidine and α-naphthol-3 : 6-disulphonic acid. Solution in water or strong sulphuric acid is red. The various brands of **Geranine** (By.) and **Brilliant Geranine** (By.) are analogously constituted.

Literature.—E. P. 17333 of 1888; D. R. P. 63951; F. P. 194406; A. P. 418657; Schultz, Ber. 1889, 22, 583.

Azo Bordeaux (By.)[1]; Naphthaleneazo-α-naphthol-4 : 8-disulphonic acid
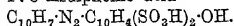
$$C_{10}H_7\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$

Prepared by the action of diazotised α-naphthylamine on α-naphthol-4 : 8-disulphonic acid. Magenta-red aqueous solution is not changed by acids or alkalis. Solution in strong sulphuric acid is blue, becoming magenta-red on dilution.

Literature.—E. P. 15775 and 15781 of 1885; D. R. P. 40571, 42304; A. P. 333035.

Azocochineal (By.); Anisoleazo-a-naphthol-4 : 8-disulphonic acid

$$CH_3\cdot O\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot OH.$$
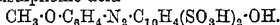
Similarly prepared from diazotised *o*-anisidine. Solution in water and strong sulphuric acid is red.

Literature.—E. P. 15775 of 1885; D. R. P. 40571.

Chromotrope 2 R (M.); **Biebrich Acid Red 4 B** (K.); **XL Carmoïsine R** (H.); Benzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $C_6H_5\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Produced from diazotised aniline and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Gives in water a magenta-red, and in strong sulphuric acid a ruby-red solution.

Literature.—E. P. 9258 of 1890; D. R. P. 69095; F. P. 206439; A. P. 458283.

Chromotrope 2 B (M.); *p*-Nitrobenzeneazo-1 : 8 - dihydroxynaphthalene - 3 : 6 - disulphonic acid $NO_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the action of diazotised *p*-nitroaniline on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is yellowish-red, and in strong sulphuric acid dark violet.

Literature.—As under Chromotrope 2R.

Victoria Violet 4 BS (M.); *p*-Aminobenzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $NH_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Prepared by the alkaline reduction of chromotrope 2 B or by eliminating the acetyl group from chromotrope 6 B (*see* below). It gives a dark-violet solution in water, and a bluish-red in strong sulphuric acid. Similar colouring matters are **Victoria Violet 8 BS** (M.) and **Azo Acid Blue B** (M.).

Literature.—E. P. 8270 of 1892; D. R. P. 70885, 73321; F. P. 221363.

Chromotrope 6 B (M.); **XL Fuchsine 6 B** (H.); *p*-Acetylaminobenzeneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid

$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2.$$
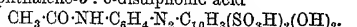
Prepared by the action of diazotised acetyl-*p*-

[1] No longer manufactured under the name 'Buffalo Rubin' by the Schöllkopf Co.

phenylenediamine on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is violet-red, and in strong sulphuric acid ruby-red

Literature.—D. R. P. 75738.

Chromotrope 10 B (M.); Naphthaleneazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $C_{10}H_7\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$.

Prepared from diazotised α-naphthylamine and the above acid. Violet solution in water, and greenish-blue in strong sulphuric acid.

Literature.—As under Chromotrope 2 R.

Chromazone Red A (G.); Benzaldehydeazo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid $CHO\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Produced from diazotised *p*-aminobenzaldehyde and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is red, and in strong sulphuric acid blue.

Literature.—D. R. P. 85233; F. P. 248519.

Chromazone Blue R (G.); Phenylethylhydrazone of the preceding colouring matter $C_6H_5(C_2H_5)N\cdot N:CH\cdot C_6H_4\cdot N_2\cdot C_{10}H_3(SO_3H)_2(OH)_2$. Prepared either by condensing chromazone red with *as*-phenylethylhydrazone or by the action of diazotised *p*-aminobenzylidenephenylethylhydrazone on 1 : 8-dihydroxy-3 : 6-disulphonic acid. Solution in water is blue-violet, and in strong sulphuric acid blue-red.
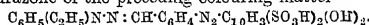
Literature as above.

Diamine Rose (C.); **Diamine Pink** (C.); Benzenylaminothiophenolazochloronaphtholdisulphonic acid

$$CH_3\cdot C_6H_4\big\langle\substack{S \\ N}\big\rangle C\cdot C_6H_4\cdot N_2\cdot C_{10}H_4Cl(SO_3H)_2\cdot OH$$
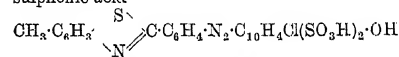
Prepared from diazotised dehydrothio-*p*-toluidine and 8-chloro-α-naphthol-3 : 6-disulphonic acid. Magenta-red solution in water, and reddish-violet in strong sulphuric acid.

Literature.—E. P. 1920 of 1894; D. R. P. 79055, 82285, 96768, 99227; F. P. 235271; A. P. 535037.

Fast Acid Fuchsine B (By.); Benzeneazo-1 : 8-aminonaphthol-3 : 6-disulphonic acid

$$C_6H_5\cdot N_2\cdot C_{10}H_3\cdot(SO_3H)_2(OH)\cdot NH_2.$$
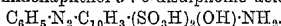
Prepared from diazotised aniline and 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) in alkaline solution. Solution in water or strong sulphuric acid is magenta-red.

Literature.—13343 of 1890; D. R. P. 62368, 70031; F. P. 210033.

Tolane Red B (K.); Benzeneazo-1 : 8-aminonaphthol-4 : 6-disulphonic acid. Isomeric with the preceding. Prepared from diazotised aniline and 1 : 8-aminonaphthol-4 : 6-disulphonic acid (K-acid). Solution in water or strong sulphuric acid is magenta-red.

Literature.—E. P. 515 of 1894; D. R. P. 99164; A. P. 563383.

Fast Sulphone Violet 5 BS (K. S.) is prepared by combining a diazo- compound with 1 : 8-aminonaphthol-3 : 6- or -4 : 6-disulphonic acid in alkaline solution, and treating the product with *p*-toluenesulphonyl chloride, whereby the amino- group is transformed into the *p*-toluenesulphonylamino- group. Other dyestuffs of the same kind are **Brilliant Sulphone Red B** (K. S.) and **Fast Sulphone Violet 4 R** (K. S.).

Literature.—E. P. 22886 of 1899; D. R. P. 120081.

Azorubine S (A.); **Azorubine A** (C.); **Azo Acid Rubine** (C. J.) (D.); **Azo Acid Rubine R** (K.); **Nacarat** (P.); **Fast Red C** (B.); **Carmoïsine** (By.); **Carmoïsine AS** (Lev.) Sulpho-α-naphthaleneazo-α-naphtholsulphonic acid
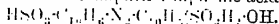
$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$$

Prepared by the action of diazotised naphthionic acid on α-naphthol-4-sulphonic acid in presence of alkali. Solution gives a red crystalline precipitate with calcium chloride; substance dissolves in strong sulphuric acid with a bluish-violet colour, becoming red on dilution. When used for after-chroming on wool the dyestuff is known as **Azochrome Blue R** (K.).

Literature.—E. P. 2237 and 4237 of 1883; D. R. P. 26012.

aphthol-5 sulph

Aqueous solution is bluish-red and gives a reddish-brown precipitate with hydrochloric acid. Substance dissolves in strong sulphuric acid with reddish-blue colour.

Fast Red E (B.) (K.); **Fast Red** (Lev.) (A.) (C.J.); Sulpho-α-naphthaleneazo-β-naphtholsulphonic acid $HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$. Isomeric with the preceding; prepared from diazotised naphthionic acid and Schäffer's β-naphthol-6-sulphonic acid. Aqueous solution claret-red; not precipitated by acids, dissolves in strong sulphuric acid with a violet colour, becoming red on dilution.

Literature.—E. P. 786 of 1878; D. R. P. 5411.

Croceine Scarlet 3 BX (By.) (K.); **Coccine 2 B** (A.); **Scarlet OOO** (H.). Isomeric with the last; prepared from diazotised naphthionic acid and Bayer's β-naphthol-8-sulphonic acid. Hot solution (concentrated) gives a crystalline magnesium salt on adding magnesium sulphate and allowing to cool; solution in strong sulphuric acid reddish-violet becoming yellowish-red on dilution.

Literature.—E. P. 2031 of 1881; D. R. P. 20402; A. P. 256376.

Double Scarlet Extra S (A.) (Lev.); **Double Brilliant Scarlet 3 R** (By.); **Double Brilliant Scarlet S** (K.); **Brilliant Ponceau 4 R** (By.); **Scarlet PR** (P.). Isomeric with the last; prepared from diazotised β-naphthylamino-6-sulphonic acid (Brönner's), and α-naphthol-4-sulphonic acid

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$$
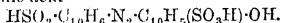
Aqueous solution gives yellowish-brown precipitate with dilute acids. Dissolves in strong sulphuric acid with a red colour, becoming yellower on dilution.

Literature.—E. P. 3724 of 1882; D. R. P. 22547.

Azofuchsine G (By.); p-Sulphobenzeneazo-dihydroxynaphthalene-4-sulphonic acid

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_4(OH)_2 \cdot SO_3H.$$
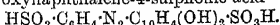
Prepared from diazotised sulphanilic acid and 1:8-dihydroxynaphthalene-4-sulphonic acid. Solution in water is bluish-red, and in strong sulphuric acid violet. Analogous colours are **Azofuchsine S** and **GN extra** (C.).

Literature.—E. P. 18517 of 1889; D. R. P. 54116; F. P. 203744; A. P. 466841, 468142.

Crumpsall Yellow (Lev.); Disulphonaphthaleneazosalicylic acid
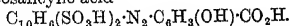
$$C_{10}H_6(SO_3H)_2 \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2H.$$

Produced by the action of diazotised β-naph-

thylamine-6:8-disulphonic acid on salicylic acid. Solution in water is yellow, and in strong sulphuric acid, orange-red.

Literature.—E. P. 12145 of 1894; D. R. P. 87483.

Lanacyl Blue BB (C.); Disulphohydroxy-naphthaleneazoaminonaphthol

$$C_{10}H_4(SO_3H)_2(OH) \cdot N_2 \cdot C_{10}H_5(OH) \cdot NH_2.$$
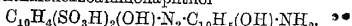
Prepared from diazotised 1:8-aminonaphthol-3:6-disulphonic acid (H-acid) and 1:5-aminonaphthol in acetic acid solution (the azo- group attacks the ortho- position relative to the hydroxy- group). Solution in water is reddish or bluish-violet, and in strong sulphuric acid blue. To this group belong also **Lanacyl Blue R** and **Lanacyl Navy Blue B** and **3 B** (C.).

Literature.—E. P. 24134 of 1896; D. R. P. 95190; F. P. 260848.

Rosophenine 10 B (Cl. Co.); **Rosophenine Pink** (Cl. Co.); **Direct Scarlet B** (K.); Sulphobenzenylaminothiocresolazo-α-naphthol-4-sulphonic acid
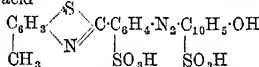
Prepared from diazotised dehydrothio-p-toluidinesulphonic acid and α-naphthol-4-sulphonic acid. Solution in water is crimson-red, and in strong sulphuric acid violet-red.

The corresponding colour from diazotised primuline is called **Rosophenine SG** (Cl. Co.); **Thiazine Red R** (B.) (D. R. P. 48465; F. P. 192628, 196988; A. P. 398990).

Thiazine Red G (B.). Prepared from diazotised primuline (sulphonic acid) and β-naphthol-6-sulphonic acid. Orange-red aqueous solution gives an orange-red precipitate with hydrochloric acid, and becomes dark with sodium hydroxide. Solution in strong sulphuric acid is blood-red, giving an orange precipitate on dilution.

References as for thiazine red R.

Dianil Yellow 2 R (M.). Prepared by the action of diazotised primuline (sulphonic acid) on 1-p-sulphophenyl-3-methyl-5-pyrazolone.

Reactions and references as for dianil yellow R.

Chrome Fast Yellow G (A.); Di-(and tri-)-sulphodiphenylphenotriazineazosalicylic acid
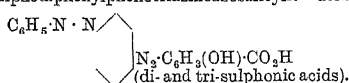
Produced from the di-(or tri-)sulphonic acids of the triazine from chrysoïdine and benzaldehyde by diazotisation and combination with salicylic acid. The aqueous solution is orange-yellow, and the solution in strong sulphuric acid is the same.

Literature.—D. R. P. 79425 (compare also D. R. P. 76491 and 78006); Noelting and Wegelin, Ber. 1897, 30, 2595.

3. TRISULPHONIC ACIDS.

New Coccine (A.) (Lev.); **Brilliant Scarlet** (C.); **Croceine Scarlet 4 BX** (K.); **Victoria Scarlet 4 R** (T. M.); **Special Ponceau** (P.); **Cochineal Red A** (B.); Sulpho-α-naphthaleneazo-β-naphthol-6:8-disulphonic acid
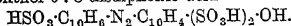
$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4 \cdot (SO_3H)_2 \cdot OH.$$

Prepared by the action of diazotised naphthionic

acid on β-naphthol-6 : 8-disulphonic acid (G-salt). . Aqueous solution red, not precipitated by acids. Dissolves in strong sulphuric acid with a red colour, becoming yellowish-red on dilution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; A. P. 314938.

Fast Red D (B.); **Azo Acid Rubine 2 B** (D.); **Fast Red EB** (B.); **Cloth Red** (T. M.); **Bordeaux S** (A.) (Lev.); **Amaranth** (M.) (C.). Isomeric with the preceding. Prepared from diazotised naphthionic acid and R-salt.

Literature.—D. R. P. 3229.

Chromotrope 8 B (M.).—*p*-Sulphonaphthalene-azodihydroxynaphthalene-3 : 6-disulphonic acid

$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_3(SO_3H)_2(OH)_2.$$
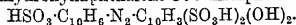
Prepared by the action of diazotised naphthionic acid on 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid. Solution in water is violet-red, and in strong sulphuric acid indigo-blue. In addition to this and the other ‘ chromotrope ’ colours mentioned above, the marks S, SB, SR, 7 B, F B, and F 4 B also appear on the market, but their constitution has not yet been published.

Literature.—E. P. 9258 of 1890; D. R. P. 69095 ; F. P. 206439; A. P. 458283.

4. TETRASULPHONIC ACIDS.

Ponceau 6 R (M.) (B.); *p*-Sulphonaphthalene-azo-β-naphtholtrisulphonic acid
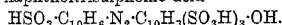
$$HSO_3 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_3(SO_3H)_3 \cdot OH.$$

Prepared by the action of diazotised naphthionic acid on β-naphthol-3 : 6 : 8-trisulphonic acid. Solution in water is magenta-red, and in strong sulphuric acid violet.

Literature.—E. P. 2544 of 1882 ; D. R. P. 22038 ; F. P. 137109 ; A. P. 268506.

Heliopurpurine 4 BL (By.); Disulphonaphthaleneazo-α-naphthol-3 : 6-disulphonic acid
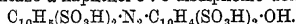
$$C_{10}H_5(SO_3H)_2 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$

Prepared from diazotised β-naphthylamine-3 : 6-disulphonic acid and α-naphthol-3 : 6-disulphonic acid. Used exclusively in the manufacture of lakes.

Literature.—Färber-Zeit. 1904, 15, 95.

Heliopurpurine 7 BL (By.) Isomeric with the preceding. Prepared by the action of diazotised β-naphthylamine-1 : 6-disulphonic acid on β-naphthol-3 : 6-disulphonic acid (R-salt). Used only for lakes.

Literature as above.

5. PENTASULPHONIC ACIDS.

Heliopurpurine GL (By.); Disulphonaphthaleneazo-β-naphthol-3 : 6 : 8-trisulphonic acid
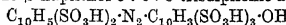
$$C_{10}H_5(SO_3H)_2 \cdot N_2 \cdot C_{10}H_3(SO_3H)_3 \cdot OH.$$

Prepared from diazotised β-naphthylamine-3 : 6-disulphonic acid and β-naphthol-3 : 6 : 8-trisulphonic acid.

Use and literature as above.

E. Carboxylic Acids of Hydroxyazo- Compounds.[1]

Alizarine Yellow GG (M.); **Chrome Yellow R**(P.); *m*-Nitrobenzeneazosalicylic acid

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$
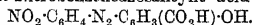
Prepared from diazotised *m*-nitroaniline and salicylic acid. The commercial product (the free acid) is a yellow paste, insoluble in water, and giving an orange solution with strong sul-

[1] Carboxylic acids containing also sulphonic acid groups are described under the corresponding sulphonic or disulphonic acids.

phuric acid. The sodium salt is put on the market in the dry state as **Alizarine Yellow GGW** (M.).

Literature.—E. P. 17583 of 1887 ; D. R. P. 44170 ; F. P. 187821 ; A. P. 424019.

Alizarine Yellow R[1] (M.) (C. R.) (By.); **Terracotta** (G.) ; **Chrome Orange** (P.) ; **Xanthochromine.** Isomeric with the last. Prepared from diazotised *p*-nitroaniline and salicylic acid. Comes on the market as a brown paste insoluble in water and giving an orange-yellow solution with strong sulphuric acid. This consists of the free acid ; the sodium salt (soluble in water with an orange colour) is called **Alizarine Yellow RW** (M.).

Literature.—Meldola, Chem. Soc. Trans. 1885, 47, 666 ; Bull. Mulhouse, 1892, 198 ; J. Soc. Chem. Ind. 1890, 9, 53 ; 1892, 11, 599 ; J. Soc. Dyers, 1889, 5, 106 ; E. P. 13920 of 1888. ·

Persian Yellow (G.); *o*-Nitrotolueneazosalicylic acid $NO_2 \cdot C_7H_6 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$. Prepared by nitrating *p*-tolueneazosalicylic acid (formerly in commerce under the name Flavazol) The commercial product is a 20 p.c. paste soluble in water to a yellow solution, and giving an orange-yellow solution with strong sulphuric acid.

Literature.—E. P. 13920 of 1888 ; F. P. 193190 ; A. P. 431297 ; Ber. 1907, 40, 4207.

Chrome Fast Yellow GG (A.) ; *o*-Anisoleazosalicylic acid $CH_3 \cdot O \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$. Prepared from diazotised *o*-anisidine and salicylic acid. In commerce as a bright-yellow paste or a yellow powder. Solution in hot water is greenish-yellow, and in strong sulphuric acid yellowish-brown.

Azoalizarine Yellow 6 G (D. H.) ; **Alizarine Yellow 5 G** (M.) ; **Tartrachromine GG** (I.). ; *p*-phenetoleazosalicylic acid

$$C_2H_5 \cdot O \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$
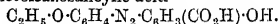
Prepared from diazotised *p*-phenetidine and salicylic acid. Solution in water is yellowish-brown, and in strong sulphuric acid brown-red.

Diamond Flavine G (By.); *p*-Hydroxydiphenylazosalicylic acid

$$OH \cdot C_{12}H_8 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$
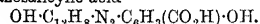
Prepared by boiling the intermediate product from tetrazotised benzidine and one molecule of salicylic acid. In commerce as a yellowish-brown paste or powder which dissolves in water only after the addition of sodium acetate. Solution in strong sulphuric acid is blood-red.

Literature.—E. P. 11663 of 1891 ; D. R. P. 60373 ; F. P. 214756.

Diamond Yellow G (By.) ; *m*-Carboxybenzeneazosalicylic acid

$$CO_2H \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$
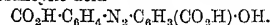
Prepared from diazotised *m*-aminobenzoic acid and salicylic acid. A greyish-yellow paste soluble in water (with addition of sodium acetate or carbonate) with a yellow colour. Gives a reddish-yellow solution with strong sulphuric acid.

Literature.—E. P. 8299 of 1889 ; D. R. P. 58271 ; F. P. 198521 (addition); A. P. 502368, 502369.

Diamond Yellow R (By.). Isomeric with the preceding. Prepared from *o*-aminobenzoic acid and salicylic acid. A brown paste soluble in

[1] **Meta Chrome Orange R double** (A.) is probably identical with this.

water (in presence of alkalis), with a yellow colour. Solution in strong sulphuric acid is reddish-yellow.

Literature as for the preceding colour.

F. Unclassified Monoazo- Colouring Matters.

Tartrazine (B.) (I.) (H.); **Hydrazine Yellow** (O.); Benzeneazopyrazolonecarboxydisulphonic acid

$$SO_3H \cdot C_6H_4 \cdot N \begin{array}{l} \diagup N = C \cdot CO_2H \\ \diagdown CO \cdot CH \cdot N_2 \cdot C_6H_4 \cdot SO_3H. \end{array}$$
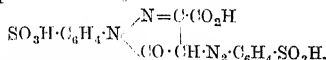
Prepared (1) by the action of p-diazobenzene-sulphonic acid on dihydroxytartaric acid; or (2) by the action of phenylhydrazinesulphonic acid on oxalacetic ester, coupling the product with diazotised sulphanilic acid and hydrolysing. Solution in water or strong sulphuric acid is yellow.

Literature.—E. P. 9858 of 1885; 5693 of 1893; 765 of 1897; D. R. P. 34294; F. P. 169964; A. P. 324630; Ziegler and Locher, Ber. 1887; 20, 834; Anschütz, Annalen, 1897, 294, 219; 1899, 306, 1; Gnehm and Benda, Annalen, 1898, 299, 100; Bernthsen, Chem. Zeit. 1898, 22, 456.

Hydrazine Yellow SO (O.) is probably a nitrotartrazine (D. P. 109914).

III. DISAZO- COMPOUNDS.[1]

A. Primary Disazo- Colouring Matters.[2]

Leather Brown (O.).:

$$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(NH_2)_2 \cdot N_2 \cdot C_6H_4 \cdot NH_2.$$
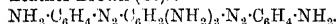
Prepared by combining 2 mols. of p-diazoacet-anilide with 1 mol. of m-phenylenediamine, and heating the product with strong hydrochloric acid. Commercial product is the mono-hydrochloride or the zinc chloride double salt. The brown aqueous solution becomes yellower on adding hydrochloric acid, and gives a brown precipitate with sodium hydroxide. The substance gives a brown solution in strong sulphuric acid, which becomes yellowish-brown on dilution.

Literature.—E. P. 11218 of 1891; D. R. P. 67429; A. P. 462414.

Terra Cotta F (G.).:

$$P^3 \cdot N_2 \cdot C_6H_2(NH_2)_2 \cdot N_2 \cdot C_{10}H_6 \cdot SO_3H.$$
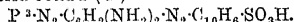
Prepared by combining first diazotised naphthionic acid and secondly diazotised primuline with m-phenylenediamine. Solution in water is brown, giving a brown precipitate with hydrochloric acid. Strong sulphuric acid dissolves colour to a reddish-violet solution, giving a brown precipitate on dilution.

Literature.—E. P. 1888 of 1890; F. P. 203439; A. P. 440288.

Cotton Orange R (B.).:

$$P^3 \cdot N_2 \cdot C_6(NH_2)_2(SO_3H)_2 \cdot N_2 \cdot C_6H_4 \cdot SO_3H.[4]$$
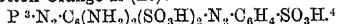
Prepared by combining first diazotised primuline and secondly diazotised metanilic acid with m-phenylenediaminedisulphonic acid. The orange-red aqueous solution gives a reddish precipitate with hydrochloric acid. Solution in

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[1] *See* also DISAZO- AND TETRAZO- COLOURING MATTERS.
[2] It will be sufficient to give the chemical formulæ of these disazo-compounds without giving their names in full.
[3] P =residue of primuline or dehydrothiotoluidine refers to sulphonic acid.
[4] According to Heumann (Die Anilinfarben und ihre Fabrikation) the formula is—
$$P \cdot N_2 \cdot C_6H(NH_2)(SO_3H)_2 \cdot NH \cdot N_2 \cdot C_6H_4 \cdot SO_3H.$$

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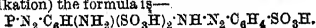
strong sulphuric acid is bright red, precipitating on dilution.

Literature.—E. P. 21753 of 1893; D. R. P. 76118; F. P. 231694; A. P. 524261.

Resorcin Brown (A.) (K.).:

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(OH)_2 \cdot N_2 \cdot C_6H_5.$$
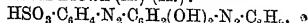
Diazoxylene chloride is combined with resorcin yellow (p. 368). Aqueous solution gives a brown precipitate with acids. Dissolves in strong sulphuric acid with a brown colour.

Literature.—D. R. P. 18862; A. P. 269359.

Fast Brown G (T. M.); **Acid Brown** (D.) (P.).

$$(HSO_3 \cdot C_6H_4 \cdot N_2)_2 C_{10}H_5 \cdot OH(\alpha).$$
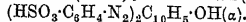
Prepared by the action of diazotised sulphanilic acid (2 mols.) on α-naphthol (1 mol.). Aqueous solution red-brown; violet precipitate with dilute acid. Strong sulphuric acid solution violet, becoming yellowish-brown on dilution.

Literature.—Krohn, Ber. 1888, 21, 3241.

Fast Brown (By.).:

$$(HSO_3 \cdot C_{10}H_5 \cdot N_2)_2 C_6H_3(OH)_2.$$
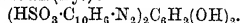
Prepared by the action of diazotised naphthionic acid (2 mols.) on resorcinol (1 mol.). Brown aqueous solution gives a readily soluble precipitate with hydrochloric acid, and becomes cherry red with sodium hydroxide. Solution in strong sulphuric acid is currant-red.

Literature.—D. R. P. 18862.

Palatine Black (B.); **Wool Black 4 B** and **6 B** (A.).:

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_3(SO_3H)(OH)(NH_2) \cdot N_2 \cdot C_{10}H_7$$

Prepared by the action of diazotised sulphanilic acid (1 mol.) on 1 : 8-aminonaphthol-4-sulphonic acid in acid solution, and treating the product in alkaline solution with diazotised α-naphthylamine (1 mol.) in alkaline solution. Dark-blue aqueous solution becomes bluish-green with hydrochloric acid and pure blue with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a dark-blue precipitate on dilution.

Literature.—E. P. 7713 of 1891; D. R. P. 91855; F. P. 213232; A. P. 590088.

Naphthol Blue Black (C.); **Naphthol Black 12 B** (C.); **Wool Black 6 G extra conc.** (T. M.); **Naphthalene Black 10 B** (P.); **Blue Black NB** (K.); **Coomassie Blue Black** (Lev.).:

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_2(SO_3H)_2(OH)(NH_2) \cdot N_2 \cdot C_6H_5$$

Prepared by the action of diazotised p-nitro-aniline (1 mol.) on 1 : 8-aminonaphthol-3 : 6-disulphonic acid (H-acid) in acid solution, and treating the product in alkaline solution with diazotised aniline. The dark-blue aqueous solution gives a blue precipitate with hydrochloric acid. The solution in strong sulphuric acid is green, giving a blue precipitate on dilution.

Literature.—E. P. 6972 of 1891; D. R. P. 65651; F. P. fourth addition to 201770; A. P. 480326.

Chrome Patent Green NC (K.)

$$(NO_2)_2C_6H_2 \cdot N_2 \cdot C_{10}H_2(SO_3H)_2(NH_2) \cdot OH \\ \underset{OH}{|} \quad \underset{N_2 \cdot C_6H_5}{|}$$
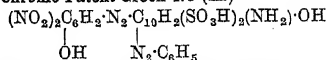
Prepared by the action of diazotised aniline (1 mol.) and diazotised picramic acid (1 mol.) on 1 : 8-aminonaphthol-4 : 6-disulphonic acid.

Literature.—D. R. P. 110711; F. P. 291316.

Blue Black N (K.)

$$(NO_2 \cdot C_6H_4 \cdot N_2)_2 C_{10}H_2(SO_3H)_2(OH) \cdot NH_2.$$
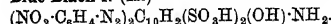
Prepared by the action of diazotised *p*-nitro-aniline (2 mols.) on 1 : 8-aminonaphthol-4 : 6-disulphonic acid.

Literature.—D. R. P. 108266; F. P. 271070; A. P. 613639.

Supramine Black BR (By.). The special base used in the preparation of this colouring matter is *p*-aminophenyl ether. Two mols (or one of this and one of another base) are diazotised and combined with 1 : 8-aminonaphthol-4 : 6- or 3 : 6-disulphonic acid.

Literature.—F. P. 402546; A. P. 958830.

Janus Yellow R (M.) :

$N(CH_3)_3Cl \cdot C_6H_4 \cdot N_2 \cdot C_6H_2(OH)_2 \cdot N_2 \cdot C_6H_4 \cdot NO_2$.

Prepared by combining diazotised *m*-aminophenyltrimethylammonium chloride with *m*-nitrobenzeneazoresorcinol.   Yellowish - brown aqueous solution gives a yellowish-brown precipitate.   Solution in strong sulphuric acid is magenta-red, becoming yellow on dilution.

Azidine Fast Scarlet G, 4 BS, 8 BS, 12 BS (C. J.). These dyes are prepared by the action of 2 mols. of a diazo- compound, for example, that from β-naphthylamine on the substance
$HSO_3 \cdot C_{10}H_5(OH) \cdot NH \cdot CO \cdot NH \cdot C_6H_2(CH_3) \cdot SO_3H$

$OH \cdot C_{10}H_5(SO_3H) \cdot NH \cdot CO \cdot NH$

Literature.—D. P. (appl.) J. 11718; F. P. 412138; A. P. (appl.) 541843.

Benzo Fast Scarlet GS, 4 BS and 8 BS (By.). These dyes are obtained by the action of 2 mols. of a diazo- compound on the urea produced by the action of carbonyl chloride on 2 mols. of 5-amino-α-naphthol-3-sulphonic acid (J-acid): *i.e.*
$HSO_3 \cdot C_{10}H_5(OH) \cdot NH \cdot CO \cdot NH \cdot C_{10}H_5(OH) \cdot SO_3H$.

Literature.—E. P. 3615 of 1900; D. R. P. 122904, 126133, 126801, 128195, 129464, 132511; F. P. 297367; A. P. 653498, 662122, 675629, 675632.

B. Secondary Disazo- Colouring Matters.

Sudan III (A.) (Ib.) (Fi.) ; **Cerasine Red** (C.) ; **Cerotine Scarlet R** (C. J.); **Fat Ponceau G** (K.). :
$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH(β)$.

Prepared by the action of diazotised aminoazobenzene on β-naphthol. Insoluble in water; dissolves in strong sulphuric acid with a green colour, becoming blue, and finally red and precipitating on dilution.

Literature.—Nietzki, Ber. 1880, 13, 1838; D. R. P. 16483.

Ponceau 5 R (M.) (K.) ; **Erythrine X** (B.) :
$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_3(SO_3H)_3 \cdot OH$.

Prepared by the action of diazotised aminoazobenzene on β-naphthol-3 : 6 : 8-trisulphonic acid in alkaline solution.

Literature.—E. P. 2544 of 1882; D. R. P. 22038; F. P. 137109; A. P. 268507.

Cloth Red G (By.) ; **Cloth Red R** (D.),
$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$.

Prepared by the action of diazotised aminoazobenzene on α-naphthol-4-sulphonic acid in alkaline solution.   Dissolves in strong sulphuric acid with a violet colour, giving a brownish-red precipitate on dilution.

Literature.—E. P. 2237 of 1883; D. R. P. 26012.

Croceïne B (Sch.). The disulphonic acid corresponding with the preceding: produced by the action of diazotised aminoazobenzene on α-naphthol-4 : 8-disulphonic acid.

Literature.—E. P. 15775 and 15782 of 1885; D. R. P. 40571; A. P. 333037.

Brilliant Croceïne M (C.) (By.) (M.) ; **Brilliant Croceïne O** (K.) ; **Brilliant Croceïne, extra conc.** (T. M.) ; **Cotton Scarlet** (B.) ; **Ponceau BO extra** (A.) ; **Croceïne 3 B** (P.) :
$C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH$.

Prepared by the action of diazotised aminoazobenzene on β-naphthol-6 : 8-disulphonic acid. Dissolves in strong sulphuric acid with a reddish-violet, becoming first bluer and then red on dilution.

Literature.—E. P. 816 of 1884; D. R. P. 36491; F. P. 159998; A. P. 314939.

Oil Scarlet (M.) (W.) ; **Red B, Oil soluble, extra conc.** (Remy.) : **Cerotine Ponceau 3 B** (C. J.); **Fat Ponceau R** (K.). (*See* also **Fast Azo Garnet**, p. 363.)
$C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_6 \cdot OH$.

Prepared from diazotised *o*-aminoazotoluene and β-naphthol. Insoluble in water, but soluble in alcohol or benzene with a bluish-red colour. Strong sulphuric acid gives a blue solution, which yields a red precipitate on dilution.

Cloth Red B (By.) (D.) :
$C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$.

Prepared by the action of diazotised *o*-aminoazotoluene on α-naphthol-4-sulphonic acid. The red aqueous solution gives a red precipitate with hydrochloric acid, and on adding sodium hydroxide to the solution it becomes violet. The solution in strong sulphuric acid is blackish-blue.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Cloth Red G (O.) ; **Cloth Red G extra** (By.) :
$C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH(β)$.

Produced by the action of diazotised aminoazotoluene on β-naphthol-6-sulphonic acid (Schäffer's).   Dissolves in water with a red-brown colour giving a similarly coloured precipitate on addition of acid. Dissolves with a blue colour in strong sulphuric acid, giving a brownish-red precipitate on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Cloth Red B (O.) (K.) ; **Cloth Red O** (M.) ; **Cloth Red BA** (A.) ; **Fast Bordeaux O** (M.) ; **Fast Milling Red B** (Lev.) :
$C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH(β)$.

Prepared by the action of diazotised aminoazotoluene on β-naphthol-3 : 6-disulphonic acid (R-salt). Aqueous solution red, becoming brownish on addition of hydrochloric acid. Dissolves in strong sulphuric acid with a blue colour, giving a brownish-red precipitate on dilution.

Literature as under preceding colour.

Cloth Red 3 G extra (By.) ; **Cloth Red 3 GA** (A.) : $C_7H_7 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_6(SO_3H) \cdot NH_2$. Prepared by the action of diazotised aminoazotoluene on β-naphthylamine-6-sulphonic acid (Brönner's acid). The red aqueous solution gives with hydrochloric acid a dark reddish-brown precipitate. The solution in strong sulphuric acid is dark greenish-blue, and gives a brownish-red precipitate on dilution.

Bordeaux BX (By.) :
$C_8H_9 \cdot N_2 \cdot C_8H_8 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$.

Prepared by the action of diazotised aminoazoxylene on β-naphthol-6-sulphonic acid

(Schäffer's). Solution in water is brownish-red, and gives a brownish-red precipitate with hydrochloric acid or sodium hydroxide. Strong sulphuric acid dissolves colour to a brown solution, which gives a reddish-brown precipitate on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Archil Red A (B.); **Union Fast Claret** (Lev.) :
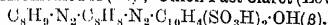
$C_6H_9 \cdot N_2 \cdot C_8H_8 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH(\beta).$

Prepared by the action of diazotised aminoazoxylene on β-naphtholdisulphonic acid (R-salt). Soluble in water with a Bordeaux-red colour ; reddish-brown flocculent precipitate on adding dilute acid. Solution in strong sulphuric acid dark blue, giving reddish-brown precipitate on dilution.

Literature.—E. P. 5003 and 5021 of 1879; 536 of 1880; D. R. P. 22010; A. P. 210233, 246221.

Croceïne Scarlet 3 B (By.) (C. J.); **Ponceau 4 RB** (A.) :
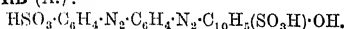
$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$

Produced by the action of diazotised aminoazobenzenesulphonic acid on β-naphthol-8-sulphonic acid (Bayer's). Solution not precipitated by alkali; a red precipitate produced by barium chloride, becoming dark-violet and crystalline on boiling. Dissolves in strong sulphuric acid with a deep-blue colour, becoming violet and then red on dilution.

Literature.—E. P. 1225 and 2030 of 1881, 2411 of 1883, 8390 of 1884; D. R. P. 18027; F. P. 142024 ; A. P. 256380.

Fast Scarlet B (K.) :
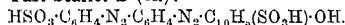
$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on β-naphthol-6-sulphonic acid (Schäffer's). Red solution in water, giving brown precipitate with hydrochloric acid and a red-violet coloration with sodium hydroxide. Solution in strong sulphuric acid is blue, and becomes red on dilution.

Literature.—D. R. P. 16482.

Cloth Scarlet G (K.) :
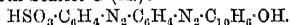
$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH.$

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on β-naphthol. The scarlet solution in water gives a brown precipitate with sodium hydroxide, and becomes yellower on addition of hydrochloric acid when dilute, but in concentrated solutions a light-red precipitate is produced. The solution in strong sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 5003 of 1879; D. R. P. 16482.

Milling Orange (D.) :
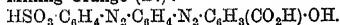
$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$

Prepared by the action of diazotised aminoazobenzenemonosulphonic acid on salicylic acid. Orange-red solution in water, giving greyish-yellow precipitate with hydrochloric acid, and a dark-red solution and precipitate with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a greyish-yellow precipitate on dilution.

Biebrich Scarlet ; Ponceau 3 RB (A.); **New Red L** (K.) ; **Imperial Scarlet** (By.) ; **Ponceau B** (M.) ; **Fast Ponceau B** (B.) ; **Double Scarlet** (K.)

$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$
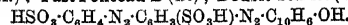
Prepared from diazotised aminoazobenzenedisulphonic acid and β-naphthol. Solution not precipitated by alkali; a brown flocculent precipitate by dilute acids. Dissolves in strong sulphuric acid with a green colour, becoming first blue and finally brown and precipitating on dilution.

Literature.—E. P. 5003 of 1879, 529 of 1887; D. R. P. 16482, 16483 ; A. P. 224927, 224928 ; Nietzki, Ber. 1880, 13, 800, 1838 ; Miller, *ibid.* 542, 803, 980.

Croceïne Scarlet O extra (K.) :
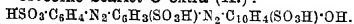
$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(SO_3H) \cdot N_2 \cdot C_{10}H_4(SO_3H) \cdot OH.$

Prepared by the action of diazotised aminoazobenzenedisulphonic acid on β-naphthol-8-sulphonic acid. The yellowish-red aqueous solution gives a violet coloration with hydrochloric acid or sodium hydroxide. The solution in strong sulphuric acid is blue, becoming yellowish-red on dilution.

Fast Ponceau 2 B (B.) :
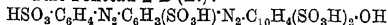
$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(SO_3H) \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH$

Prepared by the action of diazotised aminoazobenzenedisulphonic acid on β-naphthol-3 : 6-disulphonic acid (R-salt). Dissolves in strong sulphuric acid with a blue colour, becoming orange-red on dilution.

Literature.—Miller, Ber. 1880, 13, 542, 803 ; Nietzki, *ibid.* 980, 1838.

Wool Black (A.) (B.) :

$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_6H_5(SO_3H) \cdot N_2 \cdot C_{10}H_5 \cdot NH \cdot C_7H_7.$
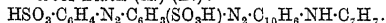
Prepared by the action of diazotised aminoazobenzenedisulphonic acid on p-tolyl-β-naphthylamine.[1] Aqueous solution gives a violet precipitate with acids. Dissolves with a blue colour in strong sulphuric acid, giving a brown precipitate on dilution, and decomposing on boiling with the formation of Acid Yellow and tolunaphthazine.

Literature.—E. P. 9754 of 1886 ; D. R. P. 38425 ; A. P. 354746.

Croceïne Scarlet 7 B ; Ponceau 6 RB (A.); **Croceïne Scarlet 8 B** (K.) (By.) :
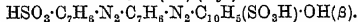
$HSO_3 \cdot C_7H_6 \cdot N_2 \cdot C_7H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH(\beta).$

Prepared by the action of diazotised aminoazotoluenesulphonic acid on β-naphthol-8-sulphonic acid (Bayer's) in presence of alkali. Resembles croceïne scarlet 3 B in general properties; gives a crystalline magnesium salt on adding magnesium sulphate to hot concentrated solution and allowing to cool. Dissolves with a blue colour in strong sulphuric acid, becoming red on dilution.

*Literature* as for croceïne scarlet 3 B ; and A. P. 256375.

Orseilline 2 B (By.). Prepared by the action of diazotised aminoazotoluenesulphonic acid on α-naphthol-4-sulphonic acid. Dissolves with a blue colour in strong sulphuric acid, becoming red on dilution.

Literature.—E. P. 2237 and 4237 of 1883 ; D. R. P. 26012.

Bordeaux G (By.). Prepared by the action of diazotised aminoazotoluenemonosulphonic acid on β-naphthol-6-sulphonic acid (Schäffer's).

Literature.—E. P. 5003 of 1879.

Bordeaux BX (By.).—

$HSO_3 \cdot C_6H_3 \cdot N_2 \cdot C_6H_7(SO_3H) \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$
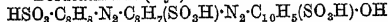
[1] Prepared by heating β-naphthol with paratoluidine and dry calcium chloride :

$C_{10}H_7 \cdot OH + C_7H_7 \cdot NH_2, HCl = C_{10}H_7 \cdot NH \cdot C_7H_7 + H_2O + HCl$

(Friedländer, Ber. 1883, 16, 2078).

Prepared by the action of diazotised aminoazo-xylenedisulphonic acid on β-naphthol-6-sulphonic acid (Schäffer's). Red aqueous solution giving reddish-brown precipitate with hydrochloric acid and becoming browner with sodium hydroxide. Strong sulphuric acid gives a dark-green solution which turns blue and finally gives a brownish-red precipitate on dilution.

Literature.—E. P. 5003 of 1879.

Eriochrome Verdone A (G.):

$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_7H_5(OH) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$
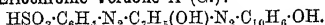
Sulphanilic acid is diazotised and combined with *m*-amino-*p*-cresol and the product is diazotised and combined with β-naphthol. The violet aqueous solution becomes claret-red with hydrochloric acid, and blue-green with sodium hydroxide. The solution in strong sulphuric acid is green, giving a brown-red precipitate on dilution. Wool is dyed in claret-red shades from an acid-bath and on chroming becomes blue-green.

Literature.—E. P. 13904 of 1909; D. R. P. 201377; F. P. 404536.

Janus Red (M.):

$N(CH_3)_3Cl \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CH_3) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$
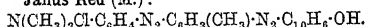
Prepared by diazotising *m*-aminophenyltrimethylammonium chloride, combining with *m*-toluidine, diazotising the product and combining with β-naphthol. The red aqueous solution gives a brownish-red precipitate with hydrochloric acid and a bluish-violet precipitate with sodium hydroxide. The solution in strong sulphuric acid is green, and gives a red precipitate on dilution.

Literature.—D. R. P. 93499.

Nyanza Black B (A.):

$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)(NH_2) \cdot OH.$
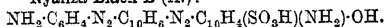
Prepared by the action of diazotised *p*-aminobenzeneazo-α-naphthylamine (only one amino-group is diazotised)[1] on 7-amino-a-naphthol-3-sulphonic acid (γ-acid). Solution is dark-violet and gives violet precipitates with hydrochloric acid and sodium hydroxide. The solution in strong sulphuric acid is blue, and gives a violet precipitate on dilution. The colouring matter itself produces only indifferent shades, but when diazotised and developed on the fibre fast shades are obtained. When developed with *m*-tolylenediamine, a brown-black is obtained, and with β-naphthol a navy-blue.

Literature.—E. P. 277 and 6630 of 1892; D. R. P. 72394; F. P. 221378; A. P. 491410, 511688, 512167.

Coomassie Wool Black R (Lev.):

$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$
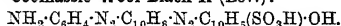
Prepared by the action of diazotised *p*-acetylaminobenzeneazo-α-naphthylamine on β-naphthol-6-sulphonic acid (Schäffer's), and hydrolysing the product. The dark-violet solution gives a precipitate with hydrochloric acid. The solution in strong sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 24980 of 1899; D. R. P. 122457; A. P. (appl.) 1764 of 1900.

Coomassie Wool Black S (Lev.):

$NH_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$
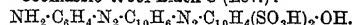
Prepared as the preceding dyestuff, the final

[1] All the authorities give the above constitution for this colouring matter, but it is generally understood that a benzenoid amino- group is diazotised preferably to a naphthalenoid amino- group.

component being β-naphthol-3 : 6-disulphonic acid (R-salt). The blue-black aqueous solution becomes redder with hydrochloric acid. The solution in strong sulphuric acid is green, becoming red on dilution.

Literature.—E. P. 24980 of 1899; D. R. P. 122457; A. P. (appl.) 1763 of 1900.

Granite Black (A.):

$OH \cdot C_6H_2(NO_2)_2 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot OH.$

Picramic acid is diazotised and combined with α-naphthylamine-6-(or 7)-sulphonic acid, and the product is diazotised and combined with β-naphthol. The dark-violet blue aqueous solution gives a dark greenish-blue precipitate with sodium hydroxide, and a dark violet-blue precipitate with hydrochloric acid. The solution in strong sulphuric acid is blackish-violet.

Literature.—E. P. 21437 of 1896; D. R. P. 113241; F. P. 260056; A. P. 583439.

Diaminogen Black (C.):

$NH_2 \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$

Monoacetyl-1 : 4-naphthylenediamine-7 sulphonic acid is diazotised and combined with α-naphthylamine, the intermediate product diazotised and combined with 7-amino-α-naphthol-3-sulphonic acid (γ-acid), and the product saponified. When diazotised and developed on the fibre a fast black is produced.

Literature.—E. P. 15443 of 1893; D. R. P. 78831; F. P. 232299; A. P. 533463.

Diaminogen Blue BB (C.).
Prepared as the preceding, but the end component is β-naphthol-6-sulphonic acid (Schäffer's).

Literature as above.

Diaminogen Blue G (C.).
Prepared as above. the end-component being β-naphthol-3 : 6-disulphonic acid (R-salt).

Literature as above.

Diazo Indigo Blue
is an analogous product.

Zambesi Sky Blue 4 B (A.).
Prepared from diazotised monoacetyl-3 : 6-diaminocresyl methyl ether combined with α-naphthylamine,[1] the intermediate product being diazotised and combined with β-naphthol-6-sulphonic acid and the end-product saponified. The reddish-violet aqueous solution becomes redder with hydrochloric acid and bluer with sodium hydroxide. The solution in strong sulphuric acid is blue and becomes violet-red on dilution.

*Literature.*—E. P. 2188 of 1901; D. R. P. 126172.

Victoria Black B (By.):

$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H) \cdot OH.$
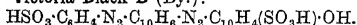
Prepared by the action of diazotised *p*-sulphobenzeneazo-α-naphthylamine on 1 : 8-dihydroxynaphthalene-4-sulphonic acid. The dark reddish-violet aqueous solution gives with hydrochloric acid a Bordeaux-red precipitate, and with sodium hydroxide becomes dark-blue violet. The solution in strong sulphuric acid is moss-green, changing on dilution to sea-green and then to bluish-red.

Literature.—E. P. 13665 of 1889; D. R. P. 61707, 62945; F. P. 200520; A. P. 466202.

Jet Black R (By.):

$(HSO_3)_2C_6H_3 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot NH \cdot C_6H_5.$
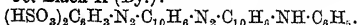
Prepared by the action of diazotised disulphobenzeneazo-α-naphthylamine on phenyl-α-naphthylamine. The bluish-violet aqueous

[1] According to Buntrock (Zeitsch. Farben-Ind. 1902 1, 224). The patents quoted give the 6- or 7-sulphonic acid as intermediate component.

solution gives a bluish-black precipitate with hydrochloric acid, and a soluble violet precipitate with sodium hydroxide. Strong sulphuric acid dissolves the colouring matter to a blue solution, which gives a greenish-blue precipitate on dilution.
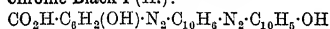
Literature.—E. P. 14442 of 1888 ; D. R. P. 48924 ; F. P. 193430 ; A. P. 425885.

Diamond Black F [1] (By.); **Chrome Fast Black B** (I.) ; **Chrome Deep Black D, extra conc.** (T. M.) ; **Salicin Black D** (K.) :

$$CO_2H \cdot C_6H_3(OH) \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$$

Aminosalicylic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with α-naphthol-4-sulphonic acid. Bluish-violet solution gives violet precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. Solution in strong sulphuric acid is greenish, giving a violet precipitate on dilution. Similar dyestuffs are **Era Blacks J, F, NG, B** and **R** (Lev.).

Literature.—E. P. 8299 of 1899 ; D. R. P. 51504 ; F. P. 198521 ; A. P. 438438.

Chrome Black I (H.):

$$CO_2H \cdot C_6H_2(OH) \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_5 \cdot OH$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad SO_3H \quad\quad\quad\quad\quad\quad\quad\quad SO_3H$$

Prepared as above, except that the starting material is the sulphonic acid of aminosalicylic acid. The red-violet aqueous solution becomes crimson with hydrochloric acid, and blue with sodium hydroxide. The solution in strong sulphuric acid is bluish-green, becoming violet on dilution.

Literature.—E. P. 2468 of 1899 ; D. R. P. 123115 ; F. P. 293923.

Nerol B (A.):

$$C_6H_5 \cdot NH \cdot C_6H_3 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4 \cdot OH$$
$$\quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad SO_3H \quad\quad\quad\quad\quad\quad\quad SO_3H$$
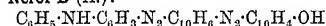
p-Aminodiphenylamine-*o*-sulphonic acid is diazotised and combined with α-naphthylamine, and the intermediate product is diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). Dark violet-blue solution in water gives a blue precipitate with hydrochloric acid. The solution in strong sulphuric acid is dark-blue violet, giving a blue-violet precipitate on dilution.

Literature.—E. P. 24527 of 1897 ; D. R. P. 101274 ; F. P. 271609.

Nerol 2 B (A.). Prepared as the preceding, except that the last component is α-naphthol-4-sulphonic acid.

Properties and literature as above.

Diamond Green (By.):

$$C_6H_3(OH) \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)(OH)_2.$$
$$\quad |$$
$$\quad CO_2H \cdot$$
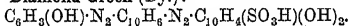
Prepared by diazotising aminosalicylic acid and combining with α-naphthylamine, the intermediate product being diazotised and combined with 1 : 8-dihydroxynaphthalene-4-sulphonic acid. The blackish-violet aqueous solution gives a dark reddish-violet precipitate with hydrochloric acid, and becomes dark blue with sodium hydroxide. The solution in strong sulphuric acid is bluish-green, becoming greenish-blue, and finally giving a blackish-violet precipitate on dilution.

[1] The yearly production of this important colouring matter is about 2,000,000 kilos.

Literature.—As for Diamond Black F ; and D. R. P. 62003.

Naphthylamine Black D (C.)(K.) ; **Deep Black D, conc.** (T. M.) ; **Naphthalene Black A** (P.); **Coomassie Wool Black D** (Lev.):

$$(HSO_3)_2C_{10}H_5 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot NH_2^?.$$
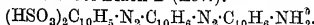
α-Naphthylamine-4 : 7-disulphonic acid is diazotised and combined with α-naphthylamine, and the intermediate product diazotised and combined with α-naphthylamine. The violet-black aqueous solution gives a black precipitate with hydrochloric acid. The solution in strong sulphuric acid is bluish-black and on dilution becomes green, and finally gives a black precipitate.

Literature.—E. P. 18425 of 1888 ; D. R. P. 50907 ; F. P. 170342 ; A. P. 412440.

Naphthylamine Black 4 B (C.) is a mixture of Naphthol blue black and the preceding colouring matter.

Naphthyl Blue Black N (C.).—Disulphonaphthaleneazo-α-naphthylamine ethyl ether is diazotised and combined with α-naphthylamine. The dark-violet aqueous solution turns blue and gives a blackish-blue precipitate with hydrochloric acid, and becomes blue and precipitates with sodium hydroxide. The solution in strong sulphuric acid is dark blue, which on dilution becomes blue, and finally bluish-violet.

Literature.—Chem. Ind. 1896, 19, 548.

Anthracite Black B (C.); **Phenylene Black** (P.):

$$(HSO_3)_2C_{10}H_5 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_6H_3(NH \cdot C_6H_5)_2.$$
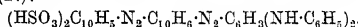
α-Naphthylamine-3 : 6-(4 : 7-in the case of the latter dye) -disulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with diphenyl-*m*-phenylenediamine. The dull-violet aqueous solution gives a violet precipitate with hydrochloric acid. The solution in strong sulphuric acid is black, giving a greenish-black precipitate on dilution.

Literature.—E. P. 4825 and 7977 of 1889 ; D. R. P. 52616, 61202 ; F. P. 196793, 197963 ; A. P. 502912.

Naphthol Black B (C.); **Brilliant Black B** (B.); **Naphthol Black OPAS** (Lev.).
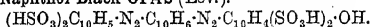
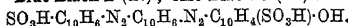$$(HSO_3)_2C_{10}H_5 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$

β-Naphthylamine-6 : 8-disulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). The violet aqueous solution gives with hydrochloric acid a reddish-violet and with sodium hydroxide a blue precipitate. The solution in strong sulphuric acid is green, becoming bluer on dilution, and then giving a reddish-violet precipitate.

Literature.—E. P. 9214 of 1885 ; D. R. P. 39029 ; F. P. 170342 ; A. P. 345901.

Naphthol Black 2 B (Lev.) is prepared as the preceding, but starting with α-naphthylamine-3 : 6-disulphonic acid.

Blue Black B (B.) ; **Azo Black O** (M.) :

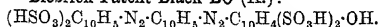$$SO_3H \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_6 \cdot N_2 \cdot C_{10}H_4(SO_3H) \cdot OH.$$

β-naphthylamine-8-sulphonic acid is diazotised and combined with α-naphthylamine, and the product diazotised and combined with β-naphtholdisulphonic acid (R-salt). Aqueous solution gives a bluish precipitate with acids

and sodium hydroxide. Solution in strong sulphuric acid bluish-green, becoming blue, and finally precipitating on dilution.

Naphthol Black 6 B (C.) (D.) (K.); Acid Black 6 B (H.); Brilliant Black BL and BD (B.); Naphthalene Black 5 B (P.) is prepared by the action of diazotised disulphonaphthaleneazo-α-naphthylamine on β-naphtholdisulphonic acid (R-salt). Aqueous solution dark violet, becoming dark blue with acid or alkali; dissolves in strong sulphuric acid with a dark-green colour, becoming blue on dilution.

Literature.—E. P. 9214 of 1885; D. R. P. 39029; F. P.170342; A. P. 345901.

Biebrich Patent Black BO (K.):

$$(HSO_3)_2C_{10}H_5 \cdot N_2 \cdot C_{10}H_5 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$
$$| \\ SO_3H$$

α-Naphthylaminedisulphonic acid is diazotised and combined with α-naphthylamine-6-(or 7)-sulphonic acid, the product diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt). The dark reddish-violet aqueous solution is turned slightly blue with hydrochloric acid, and pure blue with sodium hydroxide. Solution in strong sulphuric acid is dark greenish-blue, becoming dark violet on dilution.

Literature.—E. P. 2718 of 1892; D. R. P. 73901, 83572, 84460; F. P. 219224; A. P. 476070, 546068, 546069.

Biebrich Patent Black 4 AN (K.):
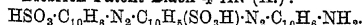
$$HSO_3 \cdot C_{10}H_8 \cdot N_2 \cdot C_{10}H_6(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot NH_2.$$

Prepared from diazotised naphthionic acid and α-naphthylamine-6-(or 7)-sulphonic acid, the product being diazotised and combined with α-naphthylamine. The violet aqueous solution gives a bluish-black precipitate with hydrochloric acid, and becomes blue with sodium hydroxide. Solution in strong sulphuric acid is bluish-green, giving a bluish-black precipitate on dilution. Similar dyestuffs bear the brands 6 AN, 4 BN, and 6 BN.

References as above.

Anthracene Acid Black (C.):
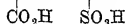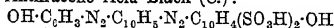
$$OH \cdot C_6H_3 \cdot N_2 \cdot C_{10}H_5 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH$$
$$| \qquad | \\ CO_2H \quad SO_3H$$

Aminosalicylic acid is diazotised and combined with α-naphthylamine-6-(or 7)-sulphonic acid, and the product diazotised and combined with β-naphthol-3 : 6-disulphonic acid (R-salt).

Naphthalene Acid Black (By.):

$$HSO_3 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot N_2 \cdot C_{10}H_6 \cdot NH_2.$$
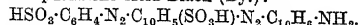
Metanilic acid is diazotised and combined with the same acid as in the preceding, and the product diazotised and combined with α-naphthylamine. Aqueous solution is violet, becoming blue with hydrochloric acid, and redder with sodium hydroxide. Solution in strong sulphuric acid is blue, becoming violet on dilution.

Sulphoncyanines are prepared from diazotised metanilic acid, which is combined with α-naphthylamine, the product being diazotised and combined with phenyl- and tolyl-α-naphthylamine-8-sulphonic acid. Dyestuffs of this class are also known as Coomassie Navy Blues 2 RNX, GNX, G and 3 R (Lev.).

Brilliant Croceïne 9 B (C.):

$$(HSO_3)_2C_{10}H_5 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$
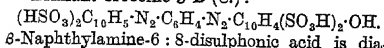
β-Naphthylamine-6 : 8-disulphonic acid is dia-

zotised and combined with aniline, the product being diazotised and combined with a mixture of β-naphthol-3 : 6- and 6 : 8-disulphonic acids. The bluish-red aqueous solution becomes darker and bluer with hydrochloric acid, and brownish with sodium hydroxide. The solution in strong sulphuric acid is blue, changing to bluish-red on dilution.

C. Tetrazo- Colouring Matters.

Anthracene Yellow C (C.):

$$S \begin{cases} C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH \\ C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH. \end{cases}$$
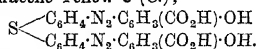
Prepared from tetrazotised thioaniline and salicylic acid (2 mols.). The light yellowish-brown aqueous solution gives a greenish-brown precipitate with hydrochloric acid. The solution in strong sulphuric acid is dark reddish-violet, giving a yellowish-grey precipitate on dilution.

Milling Red G (C.):

$$S \begin{cases} C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH \\ C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH. \end{cases}$$
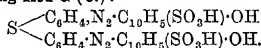
Similarly prepared from tetrazotised thioaniline and β-naphthol-6-sulphonic acid (Schaffer's). The orange-red aqueous solution gives a brown precipitate with hydrochloric acid. The solution in strong sulphuric acid is reddish-violet, giving a brown precipitate on dilution.
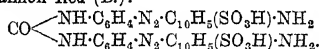
Cotton Yellow G (B.):
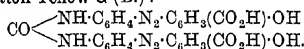
$$CO \begin{cases} NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH \\ NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH. \end{cases}$$

p-Aminoacetanilide is diazotised and combined with salicylic acid, the product hydrolysed and treated with carbonyl chloride. The yellow aqueous solution gives a brown precipitate with hydrochloric acid, and becomes rather more orange with sodium hydroxide. The solution in strong sulphuric acid is orange-red, giving a bluish-violet precipitate on dilution.

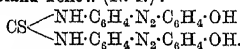*Literature.*—E. P. 15258 of 1888; D. R. P. 46737, 47902; A. P. 430535.

Salmon Red (B.):

$$CO \begin{cases} NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2 \\ NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2. \end{cases}$$

Prepared as the preceding, but naphthionic acid is used instead of salicylic acid. The orange-yellow aqueous solution gives a bluish-violet precipitate with hydrochloric acid. The solution in strong sulphuric acid is magenta-red, giving a bluish-violet precipitate on dilution.

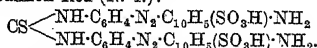*Literature.*—E. P. 14222 of 1889; D. R. P. 50852; A. P. 430534.

Heligoland Yellow (N. I.):

$$CS \begin{cases} NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH \\ NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OH. \end{cases}$$

Prepared by the action of tetrazotised di-p-aminodiphenylcarbamide on phenol (2 mols.). The yellow aqueous solution gives a brown precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. The solution in strong sulphuric acid is orange-red, giving a brown precipitate on dilution.

Literature.—D. R. P. 58204, 60152.

Salmon Red (N. I.):

$$CS \begin{cases} NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2 \\ NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2. \end{cases}$$
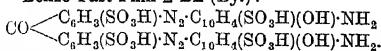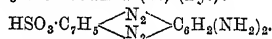
Prepared from the same tetrazo- compound as the preceding, and naphthionic acid (2 mols.).

The orange-red aqueous solution gives a bluish-violet precipitate with hydrochloric acid. The solution in strong sulphuric acid is magenta-red, giving a bluish-violet precipitate on dilution.

Literature.—As above.

Benzo Fast Pink 2 BL (By.):

$$CO\diagdown^{C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2}_{C_6H_3(SO_3H)\cdot N_2\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2}.$$

Prepared from tetrazotised di-*p*-aminodiphenyl-carbamidedisulphonic acid and 7 - amino - α - naphthol-3-sulphonic acid (γ-acid; 2 mols.). The red aqueous solution becomes reddish-violet with hydrochloric acid and yellower with sodium hydroxide. The solution in strong sulphuric acid is blue, giving an almost black precipitate on dilution.

Literature.—D. R. P. 129388, 131513; Zeitsch. Farben.-Ind. 1902, 1, 192; Chem. Zeit. 1902, 26, 485.

Bismarck Brown (most firms); **Manchester Brown**; **Phenylene Brown**; **Vesuvine**; **Leather Brown**; **Cinnamon Brown**; **English Brown**; **Brown A** (P.):

$$(NH_2)_2C_6H_3\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(NH_2)_2.$$
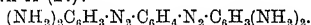
Prepared by adding a solution of 42·5 kilos. of sodium nitrite and 127·5 kilos. of hydrochloric acid to a solution of *m*-phenylenediamine prepared by reducing 250 kilos. of *m*-dinitrobenzene. The commercial product is the hydrochloride. The aqueous solution gives a brown precipitate with sodium hydroxide. The solution in strong sulphuric acid is brown, becoming red on dilution.

Literature.—E. P. 3307 of 1863; Zeitsch. f. Chem. 1867, 3, 287; Ber. 1897, 30, 2111, 2203, 2899.

Azo- Alizarine Bordeaux W (D. H.):

$$CO_2H\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.$$

p-Aminoacetanilide is diazotised and combined with salicylic acid, the product hydrolysed and diazotised and combined with α-naphthol-4-sulphonic acid. The aqueous solution is red, and that in strong sulphuric acid is blue.

Literature.—E. P. 1033 of 1899; F. P. 284775; A. P. 631089.

Azo- Alizarine Black (D. H.). Prepared as the preceding, except that the end-component is 1 : 8-dihydroxynaphthalene-3 : 6-di-(or 4-mono)-sulphonic acid. The aqueous solution is violet, and that in strong sulphuric acid blue.

Literature.—E. P. 1033 of 1899; F. P. 284775; A. P. 640010, 628721.

Violet Black (B.):
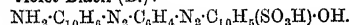
$$NH_2\cdot C_{10}H_6\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.$$

p-Aminoacetanilide is diazotised and combined with 1 mol. of α-naphthol-4-sulphonic acid. The acetyl- group is then removed by heating with acid or alkali, and the amino- compound is diazotised and combined with 1 mol. of α-naphthylamine. Aqueous solution brownish-red, giving violet precipitate with mineral acids and reddish-violet coloration with acetic acid or with sodium hydroxide; blue solution in strong sulphuric acid giving violet precipitate on dilution.

Literature.—D. R. P. 42814.

Ingrain Black C (H.):

$$HSO_3\cdot C_{10}H_5(NH_2)\cdot N_2\cdot C_6H_4\cdot C_{10}H_4(SO_3H)(OH)\cdot NH_2.$$

p-Aminoacetanilide is diazotised and combined with α-naphthylamine-6-(or 7)-sulphonic acid

(Cleve's acid), the product saponified, diazotised and combined with 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid).

Acid Alizarine Black SE (M.); **Palatine Chrome Black F** (B.):

$$HSO_3\cdot C_6H_2(OH)(N_2\cdot C_{10}H_6\cdot OH)_2.$$
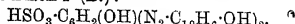
Prepared from tetrazotised 2 : 6-diaminophen-4-sulphonic acid and β-naphthol (2 mols.). Dark-blue aqueous solution gives a red precipitate with hydrochloric acid and a greenish-blue precipitate with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a red precipitate on dilution.

Literature.—D. R. P. 147880.

Manchester Brown EE (C.); **Bismarck Brown R** (H.) (W.) (L); **Bismarck Brown 2 R, extra conc.** (T. M.); **Vesuvine B** (B); **Brown N** (P.):

$$(NH_2)_2C_7H_5\cdot N_2\cdot C_7H_6\cdot N_2\cdot C_7H_5(NH_2)_2.$$
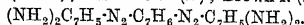
Prepared in the same manner as Bismarck brown, but *m*-tolylenediamine is used instead of *m*-phenylenediamine. The reddish-brown aqueous solution becomes yellowish-brown with hydrochloric acid, and gives a light-brown precipitate with sodium hydroxide. The solution in strong sulphuric acid is dark brown, becoming first red and then brown on dilution.

Literature.—Griess, Ber. 1878, 11, 627.

Toluylene Brown G (O.) (By.):

$$HSO_3\cdot C_7H_5\diagdown^{N_2}_{N_2}\diagup C_6H_2(NH_2)_2.$$

Prepared by the action of tetrazotised tolylene-diaminesulphonic acid ($CH_3 : NH_2 : SO_3H : NH_2 = 1 : 2 : 4 : 6$) on 1 mol. of *m*-phenylenediamine. Solution in water is brown, and in strong sulphuric acid brownish-red.

*Literature.*—E. P. 17546 of 1892; D. R. P. 65853; A. P. 516380.

Toluylene Yellow (O.). Prepared from the same tetrazo- compound as the preceding, and 2 mols. of 6-nitro-*m*-phenylenediamine in hydrochloric acid solution. The yellowish-brown aqueous solution gives brown precipitates with hydrochloric acid and sodium hydroxide. The solution in strong sulphuric acid is brown.

Literature.—E. P. 1331 of 1896; D. R. P. 86940.

Toluylene Orange RR (O.). Prepared from the same tetrazo- compound as before, and 2 mols. of β-naphthylamine. The yellowish-red aqueous solution gives a brownish-red precipitate with hydrochloric acid, and a yellowish-red precipitate with sodium hydroxide. The solution in strong sulphuric acid is bluish-grey.

*Literature.*—E. P. 17546 of 1892; D. R. P. 70147; A. P. 497032.

Diamine Gold (C.):

$$C_2H_5\cdot O\cdot C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot N_2\cdot C_6H_4\cdot OH.$$
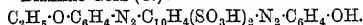
Prepared from tetrazotised 1 : 5-naphthylene-diamine-3 : 7-disulphonic acid and phenol (2 mols.), the product then being ethylated. The yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid and a yellow precipitate with sodium hydroxide. The solution in strong sulphuric acid is reddish-violet, becoming green and then yellow on dilution.

*Literature.*—E. P. 15346 of 1890; D. R. P. 61174; F. P. 182063; A. P. 472121.

Naphthylene Violet (C.):

$$NH_2\cdot C_{10}H_6\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot N_2\cdot C_{10}H_6\cdot NH_2.$$
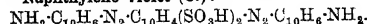
Prepared from the preceding tetrazo- compound and α-naphthylamine (2 mols.). The Bordeaux-red aqueous solution gives a blue precipitate with hydrochloric acid, and a red precipitate with sodium hydroxide. The solution in strong sulphuric acid is blue, and gives a violet precipitate on dilution. The colouring matter is usually diazotised and developed on the fibre or treated on the fibre with nitrous acid, the latter colour being known as **Diamine Cutch,** which is a fast brown shade.

Literature.—E. P. 15346 of 1890; D. R. P. 62075; F. P. 208526; A. P. 464566.

Coomassie Navy Blue (Lev.).—

$(HSO_3)_2C_{10}H_4(OH)\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot N_2\cdot C_{10}H_6'\cdot OH.$
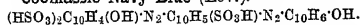
Prepared by diazotising 1 : 4-naphthylene-diamine-2-sulphonic acid (only one amino-group can be diazotised), combining with β-naphthol-3 : 6-disulphonic acid, diazotising the product (the second amino- group can now be diazotised), and combining with β-naphthol. Dark-blue aqueous solution becomes violet with sodium hydroxide. Solution in strong sulphuric acid is blue - green, becoming dark blue on dilution.

Literature.—E. P. 2946 of 1896; D. R. P. 102160; F. P. 256862; A. P.619194, 639748.

Diphenyl Fast Black[1] (G.):

$NH<^{C_7H_6\cdot N_2\cdot C_{10}H_4(OH)(NH_2)\cdot SO_3H}_{C_7H_6\cdot N_2\cdot C_7H_5(NH_2)\ldots}$
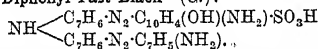
Prepared from tetrazotised *p*-diaminoditolyl-amine and 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) and 1 mol. of *m*-tolylene-diamine. The violet-black aqueous solution gives with hydrochloric acid a bluish-black precipitate, and with sodium hydroxide a black precipitate. The solution in strong sulphuric acid is dark blue, and gives a black precipitate on dilution.

Literature.—E. P. 16582 of 1896; F. P. 258521; A. P. 575904.

Dianthine (Claus & Co.); **St. Denis Red** (P.); **Rosophenine 4 B** (Cl. Co.); **Rosanol 4 B** (K.):

$O<^{N\cdot C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH}_{N\cdot C_7H_6\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.}$
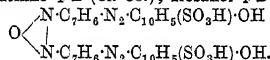
Prepared from tetrazotised diaminoazoxytoluene and α-naphthol-4-sulphonic acid (2 mols.). The red aqueous solution gives red precipitates with hydrochloric acid and sodium hydroxide. The solution in strong sulphuric acid is red, and gives a red precipitate on dilution.

Literature.—E. P. 9315 of 1887, 5736 of 1890; D. R. P. 44045; F. P. 184549; Compt. rend. 1901, 132, 985.

Congo Orange G (A.):

$C_6H_4\cdot N_2\cdot C_6H_4\cdot O\cdot C_2H_5$
$C_6H_4\cdot N_2\cdot C_{10}H_4(SO_3H)_2\cdot NH_2.$

Prepared from tetrazotised benzidine[2] and 1 mol. of β-naphthylamine-3 : 6-disulphonic acid, and 1 mol. of phenol, the product being ethylated. The orange-yellow aqueous solution gives a brown precipitate with hydrochloric acid. The

solution in strong sulphuric acid is blue, becoming reddish-violet on dilution, and finally giving a brown precipitate. The corresponding colouring matter from tolidine is **Congo Orange R** (A.).

Literature.—E. P. 17957 of 1889; D. R. P. 52328.

Pyramidol Brown BG (P. L.):

$C_6H_4\cdot N_2\cdot C_6H_3(OH)_2$
$C_6H_4\cdot N_2\cdot C_6H_3(OH)_2.$

Prepared from tetrazotised benzidine and resorcinol (2 mols.). The orange-brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes Bordeaux-red with sodium hydroxide. The solution in strong sulphuric acid is reddish-violet, giving a brown precipitate on dilution. Cotton dyed red with this colouring matter is converted into a deep brown when treated with a diazo- compound on the fibre.

Chrysamine G (By.) (A.) (Lev.) (H.); **Azidine Yellow G** (C. J.):

$C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H$
$C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H.$
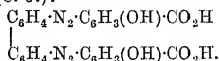
Prepared by the action of tetrazotised benzidine on salicylic acid (2 mols.) in alkaline solution. Used for dyeing cotton goods yellow directly from a soap-bath. Aqueous solution orange, becoming redder on addition of sodium hydroxide; orange flocculent precipitate, with dilute sulphuric acid. Soluble in strong sulphuric acid, with a magenta-red colour, becoming orange and precipitating on dilution. The homologue from tetrazoditolyl is **Chrysamine R.**

*Literature.*—E. P. 9162 and 9606 of 1884; D. R. P. 31658; A. P. 329638.

Cresotine Yellow G (A.) (By.) (O.):

$C_6H_4\cdot N_2\cdot C_7H_5(CO_2H)\cdot OH$
$C_6H_4\cdot N_2\cdot C_7H_5(CO_2H)\cdot OH.$
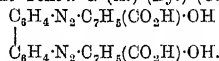
Prepared from tetrazotised benzidine and hydroxytoluic acid (OH : CH_3 : CO_2H = 1 : 2 : 6). Yellow aqueous solution gives a brownish-yellow precipitate with hydrochloric acid and becomes yellowish-red with sodium hydroxide. Solution in strong sulphuric acid is reddish-violet, precipitating on dilution. The corresponding colouring matter from tolidine is **Cresotine Yellow R** (A.) (By.) (O.); **Azidine Yellow R** (C. J.).

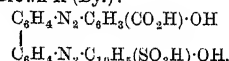*Literature.*—E. P. 7997 of 1888; A. P. 394841.

Cloth Orange (By.):

$C_6H_4\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH$
$C_6H_4\cdot N_2\cdot C_6H_3(OH)_2.$
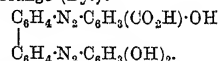
Prepared from diazotised benzidine and 1 mol. each of salicylic acid and resorcinol. Yellowish-brown solution gives brown precipitate with hydrochloric acid, and becomes red with sodium hydroxide. Solution in strong sulphuric acid is reddish-violet, giving a brown precipitate on dilution.

*Literature.*—E. P. 2213 of 1886 and 6687 of 1887; D. R. P. 44797.

Cloth Brown R (By.):

$C_6H_4\cdot N_2\cdot C_6H_3(CO_2H)\cdot OH$
$C_6H_4\cdot N_2\cdot C_{10}H_5(SO_3H)\cdot OH.$

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[1] **Diamine Deep Black** (C.) is derived from *p*-diaminodiphenylamine; **Pluto Black** (By.) also belongs to the same class.

[2] Benzidine or *p*-diaminodiphenyl is prepared by reducing nitrobenzene with zinc-dust and alkali to hydrazobenzene and converting this by means of acids into benzidine. The homologues of benzidine are prepared in a similar manner.

Prepared from tetrazotised benzidine, and 1 mol. each of salicylic acid and α-naphthol-4-sulphonic acid. Reddish-brown aqueous solution gives a brown precipitate with hydrochloric acid. Solution in strong sulphuric acid is bluish-violet, giving a reddish-brown precipitate on dilution.

Literature.—As for the preceding.

Cloth Brown G (By.):

$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$$
$$C_6H_4 \cdot N_2 \cdot C_{10}H_5(OH)_2.$$
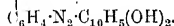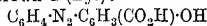
Prepared from tetrazotised benzidine and 1 mol. of salicylic acid and 1 mol. of 2 : 7-dihydroxy-naphthalene (the latter combined in weak acetic acid solution). The brown aqueous solution gives a brown precipitate with hydrochloric acid, and becomes reddish-brown with sodium hydroxide. The solution in strong sulphuric acid is reddish-violet, giving a brown precipitate on dilution.

Literature.—As for **Cloth Brown R.**

Benzo Orange R (By.):

$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$$
$$C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2.$$
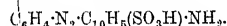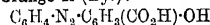
Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and naphthionic acid. The orange-yellow aqueous solution becomes reddish-violet with hydrochloric acid, and gives a reddish-yellow precipitate with sodium hydroxide. Solution in strong sulphuric acid is violet-blue, giving a greyish-violet precipitate on dilution.

Literature.—E. P. 2213 of 1886; D. R. P. 44797; A. P. 447303.

Diamine Fast Red F (C.); **Dianol Fast Red F** (Lev.) **Azidine Fast Red F** (C. J.); **Oxamine Fast Red F** (B.); **Naphthamine Red H** (K.):

$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot NH_2$$
$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$
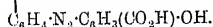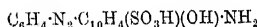
Prepared from tetrazotised benzidine and 1 mol. of 7-amino-α-naphthol-3-sulphonic acid (γ-acid) combined in acid solution, and 1 mol. of salicylic acid. Red aqueous solution gives a brown precipitate with hydrochloric acid. The solution in strong sulphuric acid is reddish-blue, and gives a brown precipitate on dilution.

Literature.—E. P. 16699 of 1889; D. R. P. 57857; F. P. 201770.

Crumpsall Direct Fast Red R (Lev.):
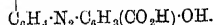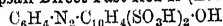
$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH$$
$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH.$$

Prepared from tetrazotised benzidine and 1 mol. each of β-naphthol-3 : 6-disulphonic acid (R-salt) and salicylic acid.

Diamine Brown M (C.); **Chlorazol Brown M** (H.); **Renol Brown MB, conc.** (T. M.); **Azidine Brown M** (C. J.); **Naphthamine Brown H** (K.); **Crumpsall Direct Fast Brown B** (Lev.):

$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$$
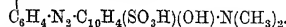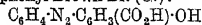$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot NH_2.$$
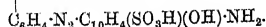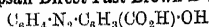
Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-amino-α-naphthol-3-sulphonic acid (γ-acid); the latter being combined in alkaline solution. The reddish-

brown aqueous solution gives a brown precipitate with hydrochloric acid and a reddish-brown precipitate with sodium hydroxide. The solution in strong sulphuric acid is violet, changing to brown on dilution.

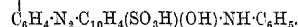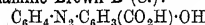*Literature.*—D. R. P. 57857; F. P. 201770.

Diphenyl Brown BN (G.):

$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$$
$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot N(CH_3)_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-dimethylamino-α-naphthol-3-sulphonic acid. [The corresponding colouring matter from the monomethylamino-compound is **Diphenyl Brown RN** (G.).] The dark-brown solution gives a red precipitate with hydrochloric acid. The solution in strong sulphuric acid is bluish-violet, giving a red precipitate on dilution. When tolidine is used instead of benzidine, **Diphenyl Brown 3 GN** is obtained.

Literature.—E. P. 2771 of 1896; D. R. P. 103149; F. P. 250697; A. P. 567413.

Diamine Brown B (C.):

$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$$
$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot NH \cdot C_6H_5.$$

Prepared from tetrazotised benzidine and 1 mol. each of salicylic acid and 7-phenylamino-α-naphthol-3-sulphonic acid. The dark-brown aqueous solution gives a Bordeaux-red precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. The solution in strong sulphuric acid is violet, giving a brown precipitate on dilution.

Oxamine Maroon (B.):

$$C_6H_4 \cdot N_2 \cdot C_6H_3(CO_2H) \cdot OH$$
$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot NH_2.$$
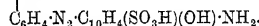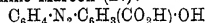
Prepared by combining tetrazotised benzidine with 1 mol. of 5-amino-α-naphthol-3-sulphonic acid in alkaline solution, and adding 1 mol. of salicylic acid to the product. The ruby-red aqueous solution does not change with acids or alkalis. The solution in strong sulphuric acid is dark violet, changing to wine-red on dilution.

Literature.—E. P. 2370 of 1893; D. R. P. 82572; F. P. 229263.

Oxamine Red (B.). Isomeric with the preceding. 6-Amino-α-naphthol-3-sulphonic acid is used instead of the 5-amino- acid. The red aqueous solution is not changed by hydrochloric acid, but becomes slightly more violet with sodium hydroxide. The solution in strong sulphuric acid is blue, changing to wine-red on dilution.

*Literature.*—E. P. 2622614 of 1893; D. R. P. 93276; F. P. 227892; A. P. 555359.

Wool Red G (B.):

$$C_6H_4 \cdot N_2 \cdot C_6H_3(SO_3H) \cdot OH$$
$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)(OH) \cdot NH_2.$$
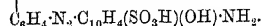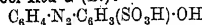
Prepared from tetrazotised benzidine and 1 mol. each of phenol-o-sulphonic acid and 7-amino-α-naphthol-3-sulphonic acid (γ-acid) the latter being combined in acid solution. The red aqueous solution gives a brown precipitate with hydrochloric acid, and becomes dark red with sodium hydroxide. Solution in strong sulphuric acid is violet, giving a brown precipitate on dilution.

*Literature.*—D. R. P. appl. 29649 of 1901 ; F. P. 313533.

Diamine Scarlet B (C.) ; **Dianil Ponceau G** (M.) [1]:

$$C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot O \cdot C_2H_5$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$
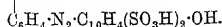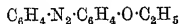
Tetrazotised benzidine is combined first with 1 mol. of β-naphthylamine-6 : 8-disulphonic acid, then with 1 mol. of phenol and the product is ethylated. The red aqueous solution becomes brownish-red with hydrochloric acid. The solution in strong sulphuric acid is violet, becoming brown on dilution.

Literature.—E. P. 12560 of 1889 ; D. R. P. 54084 ; F. P. 200152 ; A. P. 426345.

Pyramine Orange 2 R (B.):
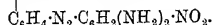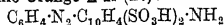
$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot NH_2$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_6H_3(NH_2)_2 \cdot NO_2.$$

Prepared from tetrazotised benzidine and 1 mol. each of α-naphthylamine-3 : 6-disulphonic acid and *p*-nitro-*m*-phenylenediamine. The yellow aqueous solution is not changed by acids or alkalis. The solution in strong sulphuric acid is blue, becoming yellowish-red on dilution.

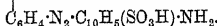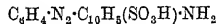*Literature.*—E. P. 6827 of 1899 ; D. R. P. 107731 ; F. P. 280914 ; A. P. 631611.

Pyramine Orange 3 G (B.):

$$C_6H_4 \cdot N_2 \cdot C_6H_2(NH_2)_2 \cdot NO_2$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_6H(SO_3H)_2(NH_2)_2.$$
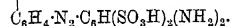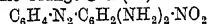
Prepared from tetrazotised benzidine and 1 mol. each of *m*-phenylenediamine-4 : 6-disulphonic acid and *p*-nitro-*m*-phenylenediamine. The yellowish-red aqueous solution is not changed by acids or alkalis. The solution in strong sulphuric acid is yellowish-red, becoming brownish-yellow on dilution.

Literature.—E. P. 18506 of 1898 ; D. R. P. 105349 ; F. P. 280914 ; A. P. 631610.

Congo Red (Lev.) (A.) (By.); **Congo Red R** (H.); **Cosmos Red** (B.); **Cotton Red conc.** (T. M.); **Cotton Red G** (P.); **Cotton Red B** (K):

$$C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2.$$

Prepared by the action of tetrazotised benzidine on naphthionic acid (2 mols). It can also be obtained by oxidising benzeneazonaphthionic acid with manganese dioxide in sulphuric acid solution (E. P. 6697 of 1895; D. P. 84893; F. P. 248210). The red aqueous solution becomes blue on addition of dilute acids ; substance dissolves in strong sulphuric acid with a slaty blue, giving a bluish precipitate on dilution.

Literature.—E. P. 4415 of 1884; D. R. P. 28753; Ber. 1886, 19, 1719.

Diazo Black B (By.). Isomeric with the preceding. Prepared from tetrazotised benzidine and α-naphthylamine-5-sulphonic acid (L-acid ; 2 mols.). The violet aqueous solution becomes blue with hydrochloric acid, and gives a blue precipitate with sodium hydroxide. The solution in strong sulphuric acid is blue, remaining blue on dilution. The colouring matter is generally diazotised and developed on the fibre.

[1] **Diamine Scarlet 3 B** (C.); **Dianil Ponceau 2 R** (M.) belongs to the same group, but is bluer.

Congo Rubine (A.) (Lev).; **Azidine Bordeaux** (C. J.):
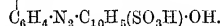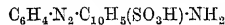
$$C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH.$$

Prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-8-sulphonic acid and naphthionic acid. The cherry-red aqueous solution gives a blue precipitate with hydrochloric acid and a violet-red one with sodium hydroxide. The solution in strong sulphuric acid is blue, giving a blue precipitate on dilution.
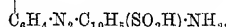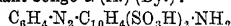
Literature.—D. R. P. 62659.

Congo Corinth G (A.) (By.); **Cotton Corinth G** (B.); **Dianil Bordeaux G** (M.):
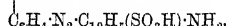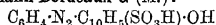
$$C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2.$$

Prepared from tetrazotised benzidine, α-naphthylamine-4-sulphonic acid and α-naphthol-4-sulphonic acid. Aqueous solution red ; violet precipitate with hydrochloric acid and coloration with acetic acid. Solution in strong sulphuric acid blue, giving violet precipitate on dilution.

Literature.—E. P. 15296 of 1885 ; 2213 and 6687 of 1886 ; D. R. P. 39096 ; F. P. 160722, 163172 ; A. P. 344971, 358865.

Brilliant Congo G (A.) (By.):

$$C_6H_4 \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot NH_2$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2.$$

From tetrazotised benzidine, β-naphthylamine-3 : 6-disulphonic acid and β-naphthylamine-6-sulphonic acid (Brönner's). Aqueous solution gives a brownish-violet precipitate with hydrochloric acid. Solution in strong sulphuric acid blue, giving violet precipitate on dilution.

*Literature.*—E. P. 6687 of 1887 ; D. R. P. 41095 ; F. P. 160722.

Heliotrope 2 B (A.) (By.) (L.):
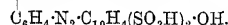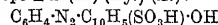
$$C_6H_4 \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot OH$$
$$\overset{|}{C_6H_4} \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH.$$

Prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-4 : 8-disulphonic acid and β-naphthol-8-sulphonic acid. Reddish-violet aqueous solution gives a bluish-violet precipitate with hydrochloric acid, and becomes redder with sodium hydroxide. Solution in strong sulphuric acid is blue, becoming reddish-violet on dilution, and finally giving a violet precipitate.

Literature.—E. P. 1346 of 1888 ; D. R. P. 45342.

Trisulphone Violet B (K. S.); **Trisulphone Blue R** (K. S.); **Trisulphone Blue B** (K. S.):

$$C_6H_4 \cdot N_2 \cdot C_{10}H_3(SO_3H)_3 \cdot OH$$
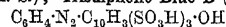
The first-named (for which the formula is given) is prepared from tetrazotised benzidine and 1 mol. each of α-naphthol-3 : 6 : 8-trisulphonic acid and β-naphthol. The second and last colouring matters are prepared from tetrazotised tolidine and dianisidine respectively instead of benzidine. The solutions in water are violet to blue, and give bluish-violet to blue precipitates with hydrochloric acid. With sodium hydroxide the aqueous solutions become reddish-violet. The solutions in strong sulphuric acid are greenish-blue, giving violet precipitates on dilution.